The influence of submarine groundwater discharge on carbon, nutrient and greenhouse gases dynamics in coastal waters

Mahmood Sadat-Noori
Southern Cross University

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THE INFLUENCE OF SUBMARINE GROUNDWATER DISCHARGE ON CARBON, NUTRIENT AND GREENHOUSE GASES DYNAMICS IN COASTAL WATERS

Authored by:
S. MAHMOOD SADAT-NOORI

Supervisors:
Professor Isaac Santos
Dr. Damien Maher
Dr. Douglas Tait

A dissertation submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy (PhD)

Lismore, Australia
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Declaration

I certify that the work presented in this thesis is, to the best of my knowledge and belief, original, except as acknowledged in the text, and that the material has not been submitted, either in whole or in part, for a degree at this or any other university.

I acknowledge that I have read and understood the University's rules, requirements, procedures and policy relating to my higher degree research award and to my thesis. I certify that I have complied with the rules, requirements, procedures and policy of the University (as they may be from time to time).

Mahmood Sadat-Noori  
Signature  
2/06/2017  
Date
Acknowledgement

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Preface

This thesis is comprised of six chapters, four of which are published in scientific journals and one in submission. **Chapter 1** is an introduction to the thesis which reviews the current knowledge of the relative field. **Chapter 2** quantifies deep fresh and shallow saline submarine groundwater discharge (SGD) into an estuarine system utilising natural geochemical tracers and introduces a new strategy in that reduces the overall uncertainty in quantifying SGD in such environments. This work has been published in *Journal of Hydrology* with the title “Groundwater discharge into an estuary using spatially distributed radon time series and radium isotopes” (*Journal of Hydrology*: 528, 703-719). **Chapter 3** quantitatively investigates the role of fresh and saline groundwater discharge determined in chapter 2 on the carbon cycling within that estuary and how groundwater can influence surface water CO$_2$ and CH$_4$ evasion rate. The results of this chapter have been published in the *Estuaries and Coasts* journal under the title “Groundwater discharge as a source of dissolved carbon and greenhouse gasses in a subtropical estuary” (*Estuaries and Coasts*: 39 (3), 639-656). **Chapter 4** examines the contribution of fresh and saline groundwater discharge on surface water quality by quantifying the role of each groundwater source in delivering nutrients to estuarine surface water. Outcomes of this chapter are published in the *Science of the Total Environment* journal under the title “Fresh meteoric versus recirculated saline groundwater nutrient inputs into a subtropical estuary” (*Science of The Total Environment*: 566-567, 1440-1453). **Chapter 5** examines the role of groundwater on coastal lake hydrology using radon as natural radio-isotope tracer. This work has been published in journal of hydrology with the title “Intermittently closed and open lakes and/or lagoons (ICOLLS) as groundwater-dominated coastal systems: Evidence from seasonal radon observation” (*Journal of Hydrology*: 535, 612-624). **Chapter 6** investigates whether submarine groundwater discharge has a major role in greenhouse gas emissions in a harbour system. This work is currently in press with the *Estuarine, coastal and Shelf Science* journal and has the title “Greenhouse Gases and Submarine Groundwater Discharge in a Sydney Harbour Embayment (Australia)”. Additionally, previously published articles that I have co-authored during the time of my PhD appear in their published format in the Appendix.
Papers published and included in the main body of the thesis:


Additional publications that are included in Appendix 1 that represent related significant work undertaken during the course of the thesis:


Statement of contribution

Published and included in the main body of the thesis:


I co-designed the project, performed field work (data collection), analysed and interpreted the data and wrote the original manuscript.


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Additional publications that are included in Appendix 1 that represent related significant work undertaken during the course of the thesis:

I performed field work (data collection) and edited the original manuscript.


I performed field work (data collection) and edited the original manuscript.

Principal supervisor name: Professor Isaac Santos
Signature and date: [Signature] 02/06/2017

Name: Mahmood Sadat-Noori
Signature and date: [Signature] 02/06/2017
Abstract

Groundwater may be highly enriched in dissolved carbon, greenhouse gases, and nutrient species, but its role as a source of these dissolved constituents to coastal waters is still poorly constrained. Moreover, assessing the relative importance of fresh versus saline groundwater-derived carbon and nutrient inputs to estuaries and how these groundwater pathways may alter surface water N:P ratios is difficult, thus understudied. This is due to the large temporal and spatial variability in groundwater discharge which makes any quantitative investigations challenging. To help close these hydrologic and biogeochemical knowledge gaps, I quantified groundwater discharge into coastal surface water bodies using radon (\(^{222}\)Rn) and radium isotopes (\(^{223}\)Ra, \(^{224}\)Ra and \(^{226}\)Ra) as natural groundwater tracers with high temporal resolution measurements. I applied these techniques in a small subtropical estuary, an embayment (large estuary) and coastal lake systems. I then used these data to quantitatively assess the role of groundwater on carbon, nutrient and greenhouse dynamics in coastal environments. I also developed a three-endmember mixing model based on short-lived radium isotopes (\(^{223}\)Ra and \(^{224}\)Ra) to separate the shallow saline and deep fresh sources of the discharging groundwater into the small estuary and quantitatively assessed the contribution of each groundwater component to carbon, nutrient and greenhouse gases inputs to surface waters.

Furthermore, I developed a new \(^{222}\)Rn sampling strategy by simultaneously applying multiple \(^{222}\)Rn time series measuring stations along a small estuary. This approach helped to reduce the spatial and temporal variability of groundwater discharge and the overall uncertainty in the estimated groundwater discharge rate. Based on the results from this sampling strategy, groundwater discharge was found to have a major contribution to carbon export, CO\(_2\) and CH\(_4\) evasion from estuary surface waters and nutrient delivery to the coastal ocean. Additionally, a radium mixing model revealed that the portion of fresh and saline groundwater discharging into the estuary changes significantly based on hydrological conditions. Specifically, in wet conditions, deep fresh groundwater discharging into the estuary contributed 65% of all groundwater compared to the shallow saline groundwater contributing only 35%, while during dry conditions a larger contribution (80%) was related to shallow groundwater.

Groundwater discharge also was a key driver in delivering dissolved organic nutrient (DON) and dissolved inorganic nutrients (DIN) to estuary surface water and a major
contributor to the large DON and DIN export form the estuary. The contribution of deep fresh groundwater discharge in delivering inorganic nutrients was significant especially at low tide in the wet season and therefore had the ability to change surface water N:P ratios on a tidal time scale. Moreover, the small estuary exported 7-times more DIN and 2-times more DIP than the global average riverine DIN and DIP export, respectively indicating that small estuaries may disproportionally contribute to nutrient exports to the nearby ocean.

In a larger urbanized estuary (embayment) groundwater discharge also was shown to be a major pathway for delivering greenhouse gases to surface waters and the atmosphere. Although CO$_2$ and CH$_4$ evasion rates observed from this larger estuary were significantly lower than those measured in the smaller estuary, which was due to seawater dilution effects, groundwater-derived greenhouse gas fluxes accounted for >100% CO$_2$ and N$_2$O and ~ 43% of CH$_4$ surface water evasion, indicating groundwater discharge is likely an important source of greenhouse gases to the estuary (embayment).

Finally, I investigated the role of groundwater on the hydrology of coastal lakes/lagoons that alternate between being connected and disconnected to the ocean. These are commonly known as intermittently closed and open lakes or lagoons (ICOLLs). ICOLLs are important coastal ecosystems that can transport dissolved constituents and material from the coastal zone to the ocean however, very little is known about the role of groundwater on their hydrological cycle. Using seasonal $^{222}$Rn measurements a comprehensive seasonal dataset was collected and used to help minimize the uncertainties associated with resolving groundwater discharge rates. Results showed that about 90% of the water inputs to the ICOLLs were from groundwater, indicating that ICOLLs are groundwater dominated coastal ecosystems. Moreover, our observations demonstrated that $^{222}$Rn can be a very useful tracer in remote and unmonitored systems were hydraulic data such at groundwater level, hydraulic conductivity and aquifer thickness is unavailable for constructing hydrological models.

Overall the thesis highlights that (1) a comprehensive spatial and temporal $^{222}$Rn sampling strategy can produce groundwater discharge estimates with lower uncertainty than using a single station and provides additional insight on where groundwater enters surface waters; (2) small subtropical estuarine systems can deliver more carbon and nutrients to the coastal waters compared to some larger riverine systems on a catchment area basis (carbon and nitrogen load divided by the catchment area); (3) groundwater discharge plays a significant role in coastal carbon, nutrient and greenhouse gas dynamics; (4) groundwater discharge plays a key role in the hydrology of ICOLLs.
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Chapter 1

Introduction
1.1 General introduction to the dissertation

Coastal ecosystems are dynamic environments due to the interaction of terrestrially-driven fresh water and saline coastal waters. This interaction can drive high productivity and biodiversity. Coastal areas are also under increasing pressure with currently more than 60% of world’s population living within 100 km of the coast and an estimated six billion to live in coastal areas by 2050 (Hameedi, 1997; Vitousek, 1997). This coastal development combined with ecosystem degradation and greater demand on ecosystem serveries such as groundwater usage has put these environments under immense pressure (Howarth et al., 2002; Seitzinger et al., 2002; Tessler et al., 2015).

Coastal ecosystems can play a major role in global carbon and nutrient cycles. For example, coastal estuarine environments are among the most productive marine ecosystems (Borges and Abril, 2011). Most estuaries are heterotrophic meaning there are higher amounts of respiration than net primary productivity which results in estuarine waters being supersaturated with CO₂ (Borges and Abril, 2011; Chen et al., 2012). Therefore, most estuaries are known to be a source of CO₂ to the atmosphere (Bauer et al., 2013). In addition to in situ respiration of organic carbon, high levels of CO₂ evasion to the atmosphere can occur due to lateral transport of dissolved organic carbon (DOC) from rivers and coastal wetlands and also CO₂-riched groundwaters (Cai et al., 1998; Cai et al., 2003; Cai et al., 2011; Atkins et al., 2013; Sadat-Noori et al., 2016).

Until recently, surface water inputs were considered the major source of constituents to the coastal ocean (Fichot and Benner, 2014). Therefore, dissolved chemical inputs from surface water ways such as rivers received a great amount of attention resulting in surface water exports being well studied and known (Seitzinger et al., 2010; Holmes et al., 2012). Submarine groundwater discharge (SGD) is now recognized as an important component of the coastal hydrological cycle (Moore, 2010). However, the role of groundwater discharge in delivering solutes and dissolved gases into the coastal surface waters is poorly constrained (Charette and Sholkovitz, 2006; Beck et al., 2009; Su et al., 2014; Call et al., 2015). Although groundwater discharge rates to coastal environments are relatively small due to the mainly diffusive nature of these flows, but because it occurs on a large scale of surface area and high concentrations of constituents in groundwater, it can be a significant nonpoint source of constituents to the ocean (Peterson et al., 2009).
The definition of SGD in the coastal context is any water within the pore spaces in the sediment that seeps into surface waters (Moore, 2010). Therefore, the discharging groundwater can include a fresh terrestrial-derived component, that is composed of rainfall infiltrating into sediments, and a saline marine component which is ocean water recirculated through the sediments (Moore, 2010). The contribution of these two components to the overall SGD flux may vary based on the forces driving groundwater discharge such as hydraulic gradient, tidal forcing, convection and bio-irrigation (Martin et al., 2006; Taniguchi et al., 2006; Santos et al., 2012). These conditions may operate on a seasonal time scale and are significantly regulated by wet and dry conditions (Michael et al., 2005). Each of the components has a distinctly different chemical characteristic and discharge rate, which produces a specific geochemical signature (Goñi and Gardner, 2003; Martin et al., 2007). Understanding this geochemical signature will usually provide insights on how the discharging groundwater will affect the quality and quantity of coastal surface waters bodies (Moore, 2006).

Recent studies have reported that there is a substantial flow of terrestrial carbon to marine environments through subsurface pathways (Porubsky et al., 2014; Faber et al. 2014; Wang et al. 2015; Stewart et al, 2015). SGD is now recognized as a major pathway for carbon and nutrient transport from terrestrial to marine environments however, quantifying groundwater inputs to coastal waters still remains a very challenging process (Porubsky et al., 2014). Even with advances in technology that have facilitated groundwater discharge measurements in recent years, quantifying groundwater is associated with a lot of spatial and temporal uncertainty (Porobsky et al, 2014). As a consequence, groundwater inputs are the least constrained component of the global nutrient and carbon budgets in coastal environments.

The concentration of nutrients in groundwater can be several orders of magnitude higher than nutrient concentrations in surface water. Therefore, even a small volume of SGD flux may deliver significant loads of nutrients to coastal surface waters (Martin et al., 2002; Santos et al., 2009). This process of delivering nitrogen and phosphorus can affect surface water quality as SGD has the ability to change N:P ratios which are a strong controller of phytoplankton growth (Howarth, 1988). Moreover, nitrogen and phosphorus are key nutrients in regulating ecosystem process in estuaries (Galloway et al., 2004) and with fresh and saline SGD delivering organic and inorganic nutrients to estuaries, groundwater discharge can play a key role in determining which nutrient is limiting primary productivity. However, very few
studies have investigated the role of different groundwater sources (e.g. fresh vs. saline) of nutrient in the nutrient cycle in estuaries.

The carbon cycle is closely related to the nitrogen and phosphorous cycles as biologically available carbon is essential for some nitrogen cycling processes to proceed and the availability of nitrogen and phosphorous for primary production may potentially lead to an increase in greenhouse gas emissions (Gruber and Galloway, 2008). Coastal estuarine ecosystems are considered hot spots for greenhouse gas production and consumption. Methane (CH$_4$), nitrous oxide (N$_2$O) and carbon dioxide (CO$_2$) are the main anthropogenic greenhouse gases, with CH$_4$ and N$_2$O being up to 96 and 250 times more potent than CO$_2$ in terms of global warming potential (Neubauer and Megonigal, 2015). Therefore, even a small amount of emission may substantially increase global anthropogenic greenhouse gas forcing (IPCC, 2013). Coastal estuarine environments are thought to play a major, yet unquantified role in the global greenhouse gas budgets (Bange, 2006). For example, coastal estuarine ecosystems have the ability to store large amounts of carbon in the soil through CO$_2$ sequestration but degradation of these ecosystems can lead to buried carbon being released into the atmosphere (Macreadie et al., 2013). Therefore, there is an increasing interest in monitoring greenhouse gases in coastal aquatic systems (DelSontro et al., 2010). Although estuarine environments have been recognized as a source of CO$_2$ and CH$_4$, the existing high temporal and spatial variability of emissions within these systems has not yet been quantitatively constrained (Abril and Borges, 2005). There are limited data available on CO$_2$ and CH$_4$ emissions from subtropical and tropical estuarine areas within the southern hemisphere, including Australia (Ortiz-Llorente and Alvarez-Cobelas, 2012).

Another important yet understudied coastal water bodies are the intermittently closed and open lakes and lagoons, commonly known as ICOLLs. The special features that make these systems unique is that they connect and disconnect to the ocean occasionally and can act as an accumulation basin which are flushed only periodically (Haines, 2006). ICOLLs are vulnerable to anthropogenic activities such as groundwater extraction, and are considered among the most sensitive estuary type to human disturbance (Boyd et al., 1992; Haines, 2006;). ICOLLs are usually considered as a surface appearance of shallow aquifers and groundwater seepage is thought to be main recharge process during most of the year (Chikita et al., 2015), therefore, minor changes in catchment and groundwater hydrology of the ICOLLs may influence their surface water quality and quantity. However, most previous studies on ICOLLs have focused on the surface water and the influence of surface water
inputs, because quantifying groundwater discharge has been seen as too complex (Chikita et al., 2015, Morris and Turner, 2011). In addition to obstacles in estimating groundwater inputs to these coastal systems, their nature of often being located in remote areas adds to the difficulties in quantifying groundwater discharge fluxes. Therefore, our knowledge about the relative contribution of groundwater seepage to ICOLL water budgets remains very limited and warrants further investigation.

1.2 Thesis aims and hypothesis

In order to address some key knowledge gaps in quantifying SGD, contribution of new (fresh) SGD, recirculated SGD to carbon dynamics and nutrient fluxes in coastal environments and investigating SGD on ICOLL hydrology, this thesis addresses the following research questions:

1. **Would using multiple radon ($^{222}$Rn) time series measurements decrease the overall groundwater discharge rate uncertainty?**

2. **Is SGD a significant source of carbon and greenhouse gases in subtropical estuaries and an important component of the global carbon cycle?**

3. **Is fresh and recirculated SGD a major pathway for nutrient delivery to small subtropical estuaries?**

4. **What is the role of groundwater discharge on the hydrology of intermittently closed and open coastal lakes or lagoons?**

5. **Is SGD a major source of greenhouse gases in large-scale estuaries such as bays?**

This thesis will add to the current literature by using a combination of modern and traditional techniques such as natural geochemical tracers, complex mass balance modelling and greenhouse gas measurement techniques (cavity ring-down spectroscopy analysis) to characterize the role of groundwater discharge on carbon and nutrient cycling in the coastal environment. I attempt this by: (1) quantitatively constraining SGD fluxes in subtropical coastal systems (Chapter 2, 5 and 6); (2) determining the contribution of fresh versus saline SGD-derived carbon and nutrients to a small subtropical estuary representing other such systems (Chapter 3 and 4); and (3) determining whether SGD plays a significant role in greenhouse gas dynamics in coastal areas (Chapters 3 and 6). I hypothesize groundwater
Discharge plays a major role in surface water biogeochemistry in coastal water with a focus on small estuaries, large embayments, and lakes, and that groundwater is an important component of the coastal carbon and nutrient cycle, greenhouse gas cycling, and a major player in coastal lake and estuary hydrology. A conceptual model illustrating the aims of the thesis is presented in Figure 1.1. In order to investigate the above questions and aims, a combination of field-based experiments and laboratory assays were performed. The fieldwork components of this thesis were performed at Hat Head, NSW, Bribie Island, QLD, and Sydney Harbour, NSW in Australia.

**Figure 1.1** A conceptual model illustrating aims and chapters of the thesis. (1) Quantifying SGD and reducing uncertainties using a spatially distributed radon (²²²Rn) time series; (2) SGD as a source of dissolved carbon, CO₂ and CH₄ in estuaries; (3) SGD as a pathway for nutrients delivery to subtropical estuaries; (4) the role of groundwater discharge on the hydrology of intermittently closed and open coastal lakes or lagoons; (5) SGD as a source of greenhouse gases in large-scale estuaries (embayments). Note: the red arrows indicate ²²²Rn gas inputs at the lower, middle, and upper parts of the estuary.
Chapter 2

Groundwater Discharge into an Estuary Using Spatially Distributed Radon Time Series and Radium Isotopes

Abstract

Quantifying groundwater discharge remains a challenge due to its large temporal and spatial variability. Here, we quantify groundwater discharge into a small estuary using radon (\(^{222}\text{Rn}\)) and radium isotopes (\(^{223}\text{Ra}\) and \(^{224}\text{Ra}\)). High temporal resolution (30 min time steps) radon observations at four time series stations were used to determine where groundwater discharge is prevalent in the estuary, and to reduce mass balance model uncertainties. A three-endmember mixing model was developed based on short-lived radium isotopes (sampled at a single location) to separate the shallow saline and deep fresh sources of the discharging groundwater. The results show that using multiple \(^{222}\text{Rn}\) time series stations decreased the overall uncertainty of groundwater discharge estimates from about 41\% to 23\%. The radon derived groundwater flux was 56±13 and 35±12 cm d\(^{-1}\) in wet and dry conditions, respectively. The spatially distributed stations detected a well-defined small area located four kilometres upstream from the mouth of the estuary as a groundwater discharging hotspot. Estimates based on a \(^{223}\text{Ra}\) and \(^{224}\text{Ra}\) mass balance resulted in groundwater discharge estimates of 65±18 and 84±48 cm d\(^{-1}\) in the wet and 18±5 and 20±6 cm d\(^{-1}\) in the dry. The mixing model revealed contrasting results for deep vs. fresh groundwater contribution in wet and dry conditions. In wet conditions, deep fresh groundwater discharging into the estuary contributed 65\% compared to the shallow saline groundwater (35\%), while during dry conditions a larger contribution (80\%) was related to shallow groundwater. A comprehensive spatial and temporal sampling strategy can produce groundwater discharge estimates with lower uncertainty and provides additional insight on where groundwater enters surface waters.

Keywords: Groundwater-surface water interaction, submarine groundwater discharge, coastal hydrology, tidal estuary, permeable sediments, mangrove.
Chapter 2 | Groundwater Discharge into an Estuary Using Spatially Distributed Radon Time Series and Radium Isotopes

2.1 Introduction

The exchange of groundwater between land and sea is an important component of the hydrological cycle. This exchange, regardless of fluid composition and driving forces is known as submarine groundwater discharge (SGD), which accounts for both fresh groundwater and recirculated seawater (Moore, 2010). SGD inputs may be volumetrically small when compared to surface runoff. However, due to the often high concentration of solutes, SGD may act as a significant pathway for pollutants and dissolved components to enter the world’s coastal oceans (Su et al., 2014). SGD is potentially an important source of carbon (Maher et al., 2013), nutrients (Santos et al., 2013), trace metals (Sanders et al., 2012, Charette and Sholkovitz, 2006, Beck et al., 2009) and greenhouse gases (Atkins et al., 2013; Porubsky et al., 2014, Perkins et al., 2015, Call et al., 2015) into surface water bodies. In some locations SGD inputs and dissolved constituents have been shown to rival those from rivers and estuaries (Slomp and Van Cappellen, 2004, Dulaiova and Burnett, 2006, Swarzenski et al., 2007), and submarine fresh groundwater discharge in coastal areas can be comparable to large river discharges (Wang et al., 2015). Despite our increased awareness of SGD importance and its significant environmental consequences, SGD has been largely understudied relative to river flow. This is mainly due to groundwater discharge being diffusive and heterogeneous spatially and temporally in complex systems where direct measurements are difficult (Crusius et al., 2005). Therefore, quantifying SGD and its inputs to coastal waters still remains a challenge (Porubsky et al., 2014).

Investigating SGD in heterogeneous systems can be achieved through the deployment of seepage meters (Burnett et al., 2006) and hydrological models (McCormack et al., 2014). Natural geochemical tracers have increasingly been used as an alternative approach to quantify SGD and investigate its effect on water budgets and water quality (Schubert et al., 2011). The main advantage of using natural geochemical tracers is that they integrate the signal related to different groundwater pathways which may be useful in spatially heterogeneous and temporally dynamic systems (Stieglitz et al., 2010, Burnett et al., 2006). Radon and radium radionuclides normally occur in higher concentrations in groundwater relative to surface water, and the decay rates of the radon ($^{222}$Rn, half-life = 3.8 days) and the short-lived radium isotopes ($^{223}$Ra and $^{224}$Ra, with half-lives of 11.4 and 3.6 days respectively) are on the same temporal scale as the physical processes usually related to groundwater discharge (Burnett et al., 2008). By assessing the $^{222}$Rn, hereafter referred to as
“radon” and radium isotopes ($^{223}$Ra and $^{224}$Ra) it is possible to estimate the amount of water SGD may contribute to coastal surface waters. This is often achieved by mass balance approaches, originally introduced by Moore (1996) and Cable et al.(1996) and refined by multiple authors over the years (Burnett et al., 2010).

While the hydraulic gradient between groundwater table and the sea surface height may cause fresh groundwater discharge, different physical process such as tidal pumping, wave setup, seasonal forcing, convection and several other processes may be the driving forces of seawater recirculation within coastal estuaries (Santos et al., 2012). Radon is an effective tracer of total (fresh and saline) SGD, while radium is often released from sediments only in the presence of brackish water due to ion exchange reactions, making it an effective tracer of recirculated saline water (Mulligan and Charette, 2006, Beck et al., 2008, Su et al., 2014). Therefore, combining radon and radium isotopes measurements may provide insight into the relative quantities of fresh and saline water in a given system (Gleeson et al., 2013).

The naturally occurring radium isotopes may be useful tools for quantifying SGD fluxes and sources. Radium is especially useful for SGD studies where subsurface mixing of fresh and saline water occurs (Moore, 2006; Charette et al., 2015). Ion exchange reactions in the mixing zone release radium into solution creating a signal that may be later identified in surface waters (Swarzenski et al., 2007; Garcia-Orellana. et al., 2014). The different half-lives of radium isotopes ranging from 3.66 days ($^{224}$Ra) to 1600 years ($^{226}$Ra) can provide insights into process taking place on different time scales (Moore, 2003). However, collecting radium samples can require the processing of large volumes of water, and significant effort in the laboratory, which may restrict the sample size.

Performing radon measurements to estimate groundwater discharge is becoming a popular method. Radon automation creates opportunities for deployments with less effort and the collection of large datasets. However, large uncertainties are still reported from different studies utilizing this approach in tidal rivers and estuaries. Previous studies have estimated uncertainties ranging from 40% to around 120% when calculating SGD using a radon mass balance (Peterson et al., 2008a, Burnett et al., 2008, Tait et al., 2013, Santos et al., 2014). Different factors within the radon mass balance have been suggested as the cause of these high uncertainties. For example, determining a groundwater endmember value may be the most important source of uncertainty (Dimova et al., 2013, Atkins et al., 2013, Peterson et al., 2010).
When using radon and radium isotopes as natural tracers for investigating SGD, either spatial surveys or time series measurements are applied. Using only one of these approaches may not provide enough information to understand exchange processes in dynamic water bodies such as shallow estuaries (Stieglitz et al., 2013, Maher et al., 2015) and can consequently increase the uncertainty. For instance, spatial surveys may be labour intensive (Stieglitz et al., 2010) and do not represent the temporal variability of chemical gradients in shallow tidal water bodies (Atkins et al., 2013). In contrast, a single time series measurement may not provide insight on exact groundwater discharge locations (de Weys et al., 2011, Burnett et al., 2010) although, it has the ability to capture temporal variability with the resolution of measurements typically at the scale of less than 1 hour. Major loss terms of the mass balance in tracer approaches are a function of transport processes between the location where groundwater enters surface waters and the location where tracer observations are made. Therefore, relying on one station in time series approaches and upscaling site specific major loss terms of the mass balance to the entire estuarine area increases the overall uncertainty. Conducting multiple time series experiments along an estuary provides data that may decrease uncertainty when solving a mass balance, but this is logistically challenging (Santos et al., 2014).

This study builds on the literature by utilizing four spatially distributed radon time series stations to estimate groundwater discharge using a radon mass balance in a small estuary. We hypothesize that using multiple radon time series stations will lead to results with less uncertainty compared to using one station, and will also provide better insight on groundwater discharge locations. Moreover, we combine the radon mass balance approach with radium isotope time series data (single station due to extensive sampling effort required for radium) in an attempt to distinguish between the contribution of deep fresh terrestrial and shallow recirculated seawater components of the total groundwater flux discharging into the estuary.

2.2 Methodology

2.2.1 Study site

Experiments were performed in Korogoro Creek, a small subtropical estuary 5 km long and about 20-25 m wide with an average depth of 0.9 m (116,160 m$^2$) in Hat Head, NSW, Australia. The study site is immediately adjacent to Hat Head National park where 50 m high
sand dunes and wetlands are located over an area of about 18 km². The tidal estuary runs approximately 400 m inland from the coastline (Figure 2.1). The terrain west of the estuary is low lying and subject to flooding by sea water during spring tides. The estuary is tidal, and ocean water penetrates the lower 4 km of the estuary at high tide. Water flowing from upstream is generally tannin-rich and brackish, and is clearly contrasted from the saline sea water that inflows during high tide. The estuary is normally completely flushed during each tidal cycle. Well sorted silt-free sands are present from the surface to depths of up to 30 m. Silty sands, silts and clays lie beneath the sands and the bedrocks are found at the depth of 60 to 80 m (Acworth et al., 2007). A sandstone layer (organically bound) exists approximately 8 meters below the estuary bed. The mixing line slope from the ocean side, stabilizes at around 13 m beneath the ground. Local and regional freshwater from both sides of the estuary and underneath it, discharge into the creek (underneath the sand dunes in between the ocean and the estuary which covers around 400 m is filled with freshwater) (Annual Groundwater Monitoring Program report, 2013).

The region has an average of 1490 mm of rain annually and experiences a mild subtropical climate all year round. The highest monthly mean temperature occurs in January at 26.9°C, and the lowest is in July at 11.2°C. Rainfall is highest from January to March (175.2 mm/month) and at its lowest from July to September (71 mm/month) (http://www.bom.gov.au). Groundwater levels in the area fluctuate up to 2 meters annually (Annual Groundwater Monitoring Program report, 2013). A sewage disposal site is located approximately two kilometers upstream from the estuary mouth. The sewage disposal is located just north of the township on the dunes between Hat Head beach and Korogoro creek (Figure 2.1). The dunes in Hat Head are undulating with shrub vegetation on the eastern side and eucalypts on the west side nearest to the estuary. The disposal site lies above a small aquifer, bounded and separated from the coastal sands aquifer by Korogoro creek and is not used for groundwater usage (Ruprecht and Timms, 2010).

2.2.2 Experimental design

This study relied on high temporal resolution data from multiple radon measuring stations along with a single radium isotope station in an estuary to quantify groundwater discharge rates. First, four radon time series monitoring stations were deployed at four fixed sites under two different hydrological conditions (only 3 stations in the season with less rain, due to vandalism), to obtain high temporal resolution radon data with spatial distribution
Chapter 2 | Groundwater Discharge into an Estuary Using Spatially Distributed Radon Time Series and Radium Isotopes

(Figure 2.1). This was done to identify groundwater discharge locations and reduce uncertainty in estimates by breaking down the estuary into smaller segments (approximately 1.5 km long). Second, deep and shallow groundwater samples were collected to characterize the groundwater endmember concentrations from various locations within the vicinity of the time series stations. The information was used to construct a segmented radon mass balance model to quantify groundwater discharge fluxes between the upstream and downstream station entering the estuary. Finally, radium isotopes were used to independently estimate groundwater discharge rates and to construct a three endmember mixing model to resolve the contribution of deep fresh and shallow saline groundwater components discharging into the estuary.

Figure 2.1 Map of study site, Korogoro creek, NSW, Australia. Radon time series stations spatial distribution at the study site and groundwater sampling locations.

2.2.3 Radon time series measurements

At each station automated radon monitors (RAD7, Durridge Co.) measured $^{222}\text{Rn}$ concentrations every 30 minutes for about 40 hours in the first campaign (wet) and 60 hours
in the second field campaign (dry). The first station (hereafter referred to as downstream) was at the mouth of the estuary (153°3'27.268"E, 31°3'24.801"S) and is considered the downstream boundary of the estuary. Station 2 was located 1.5 km upstream of station 1(153°2'35.199"E, 31°3'3.26"S) near the entrance of Hat Head township and had sandy and rocky creek banks. Station 3 was located in a mangrove environment 1.5 km upstream of station 2 (153°2'7.381"E, 31°2'29.451"S). Station 4 was deployed about 1 km upstream of station 3 (153°2'0.819"E, 31°2'10.906"S) and was considered as the upstream boundary, which was surrounded primarily by freshwater dependent vegetation.

In both the wet and dry experiments, data was collected simultaneously from the stations (all stations during the wet, all stations except station 4 during the dry). The areas between stations 1 and 2, 2 and 3, 3 and 4 and upstream of 4 are referred hereafter as box A, B, C and D respectively (Figure 2.1). The first time series campaign (wet) took place in March 2013 with the measurements starting from 08:45 pm March 25th to 10:15 am March 27th 2013, while the second field experiment (dry) was carried out in June 2013, starting from 08:30 pm June 6th to 10:00 am June 10th 2013.

For determining radon at each station, a constant stream of surface water was pumped continuously at approximately 3 L min\(^{-1}\) into a shower-head gas equilibration device (Dulaiova et al., 2005). The equilibrated air was then pumped in a closed-loop from the headspace of the equilibrator chamber through Drierite desiccant followed by a radon-in-air monitor (RAD 7, Durridge Co.). The partitioning of radon between the gas and the liquid phase was calculated as a function of temperature and salinity (Schubert et al., 2012). The radon activities are determined by counting its alpha-emitting, positively charged radioactive daughters (\(^{218}\)Po and/or \(^{214}\)Po), which are detected via a silicon detector (Schubert et al., 2006). In our case, we used \(^{218}\)Po only to ensure a short response time of about 30 min.

Three sediment core samples were taken from the study area and incubated in 60 cm long and 10 cm in diameter cylinders to estimate radon molecular diffusion from sediment. The cores were sealed and incubated with radium free water and left for a period of 1 month. This experiment was based on the assumption that after a month (> 5.5 half-lives for radon) in each core, the only source of radon (diffusion) will reach equilibrium with the only sink of radon (decay) within the core (Santos and Eyre, 2011). The overlying water in the incubation cylinders was extracted into plastic bottles and radon concentration in the water was measured using a RAD7 and closed loop system (Lee and Kim, 2006). The entire water
column was sampled from the bottom up preventing any effects of heterogeneity within the core.

2.2.4 Radium measurements

Radium samples were taken at the downstream station every hour for two low-tide to low-tide tidal cycles (~ 24 hours) by collecting 40 L of water from the estuary and filtering through manganese fibers at 1 L min\(^{-1}\) (Moore, 2010, Burnett et al., 2006). These fibers quantitatively sorb dissolved radium from the water. The filters were transported in individual bags to the lab where they were rinsed with radium free water, partially dried and placed in a Radium Delayed Coincidence Counter (RaDeCC) for measuring \(^{223}\)Ra and \(^{224}\)Ra (Moore and Arnold, 1996) with analytical uncertainties calculated following Garcia-Solsona et al. (2008). Activities of \(^{226}\)Ra were determined based on the ingrowth of radon from Mn fibers sealed in gas tight cartridges and left for at least 1 month, using the RaDeCC (Peterson et al., 2009a). The \(^{226}\)Ra data was used only as an input to the radon mass balance model (shown below).

For measuring the potential radium desorption from suspended sediments, two 40 L containers were filled with fresh water from upstream of the estuary at low tide. Marine salt was added to one of the bottles to bring the salinity up to 35 and was left for about 18 hours to allow ion exchange processes occur. Radium isotopes were then measured in fresh and salted water to estimate desorption (Peterson et al., 2008b). The experiment was repeated three times and averages are reported.

2.2.5 Ancillary data

At each site a calibrated Hydrolab automatic logger was used to measure pH, salinity, dissolved oxygen (mg L\(^{-1}\)) and water temperature (°C) at 15 min intervals. Depth loggers (CTD divers) measured estuary depth at each site. Wind speed data were obtained online (www.wunderground.com) from a weather station located at South West Rocks, NSW about 15 km away from the study site. An acoustic doppler current profiler (ADCP; Sontek Argonaut) was installed in the middle of the estuary at the downstream site to measure current velocity and direction of flow at 10 min intervals. At the three other sites current velocity was measured using Starflow Ultrasonic Doppler Flow Recorders. The estuary cross section was measured at each site at high tide. Surface water discharge was calculated by multiplying current velocity by individual time specific cross sectional areas assuming that
currents across the channel were homogenous. Discharge was measured at every station (box boundary). Estuary water volume was estimated using estuary area and the average depth of water from the 4 stations. During the second field experiment in June, we were unable to obtain any data for station 4.

2.2.6 Groundwater Sampling

Groundwater samples were collected close to surface water time series stations. At station 1, 2 and 3, three shallow wells ranging between 0.5 – 2 m deep were dug using a hand held auger at low tide. PVC pipes with 50 cm long screens attached to the end were installed to allow groundwater to infiltrate into the pipe. The transect of wells were dug at low tide mark, high tide mark and in between. In addition, we also sampled screened monitoring wells installed by the NSW Office of Water located across the catchment (Figure 2.1) to characterize the composition of the groundwater seeping into the estuary. A peristaltic pump was used to take samples after the wells were completely well flushed for three times the well volume. A calibrated handheld YSI was used to determine pH, temperature, DO and salinity for each sample. Six-liter plastic bottles were used to collect samples for radon, $^{223}$Ra, $^{224}$Ra and $^{226}$Ra analysis. These bottles are designed to prevent gas loss and radon assessment can be immediately started in the field after sampling (Stringer and Burnett, 2004). Each 6 L bottle was connected to a RAD7 radon monitor and given at least 2 hours to achieve an air-water radon equilibrium with <5% uncertainty following well established protocols (Lee and Kim, 2006). The RAD7 was purged with dry fresh air for at least half an hour before running each sample to deplete all residual radon out of the device. Additionally, the samples were bubbled for mixing the water column as they were run through the RAD7 (Lee and Kim, 2006). After radon analysis, the water was filtered through Mn fibers for radium analysis. Shallow groundwater samples were collected in the wet season whereas deep groundwater samples were collected in the dry season. To have a reasonable end-member value, the mean measurements from shallow and deep groundwater samples was used assuming minor seasonal variation in the endmember. We emphasize, however, that seasonal variability has been found for groundwater tracers at other sites (Luek and Beck, 2014). A total of 27 groundwater samples for radon and 29 samples for radium isotopes were collected from the study area in wet and dry conditions.
2.2.7 Radon mass balance

A radon mass balance model developed by Peterson et al. (2010) was adapted to estimate groundwater discharge into the estuary over a tidal cycle. The principle of using continuous radon measurement to estimate groundwater seepage relies on converting unaccounted for radon fluxes to groundwater water fluxes (Burnett and Dulaiova, 2003). A conceptual model of the radon mass balance used in this study is shown in Figure 2. The estuary was fragmented into four boxes (A, B, C and D) which communicate with each other in terms of tracer fluxes, by flood and ebb tide whereby, for example, during flood tide the flux out of box B (output) serves as an input for box C. Also, for calculating the groundwater input from box C to B the contribution of D to C is subtracted as illustrated in Figure 2.2. Additionally, flood tide from the ocean, into box A was considered a source of radon.

![Figure 2.2 Conceptual model of the radon mass balance. Positive values of flow are downstream. Estuary is 5 km long and about 20-25 m wide with distance between the 4 stations ranging from 1000 to 1500 m.](image)

The model, accounts for all known radon sinks and sources and assumes that groundwater is the missing radon source. The radon sources in this case were upstream radon flow inputs, diffusion from sediments, $^{226}$Ra decay and groundwater discharge inputs. The radon sinks were downstream radon flow, radioactive decay and radon atmospheric losses.
which are composed of wind- and current-driven evasion. The radon mass balance takes the form of:

\[ F_{gw}R_{gw} + F_{up}R_{up} + D_{dif}A + 2^{26}Ra\lambda_{222}V = F_{down}R_{down} + 2^{22}Rn\lambda_{222}V + J_{atm} \]  

(1)

where \( F_{gw} \) is the groundwater discharge (m\(^3\) s\(^{-1}\)), \( R_{gw} \) is the groundwater endmember concentration (Bq m\(^{-3}\)), \( F_{up} \) is the upstream radon flux (Bq s\(^{-1}\)), \( D_{dif} \) is radon diffusive flux (Bq m\(^2\) s\(^{-1}\)), \( A \) is the estuary surface area (m\(^2\)), \( 2^{26}Ra\lambda_{222}V \) is radium decay (Bq s\(^{-1}\)) (\( 2^{26}Ra \) is radium concentration, \( \lambda_{222} \) is radon decay rate and \( V \) is the volume of water in estuary), \( F_{down} \) is the radon downstream flux (Bq s\(^{-1}\)), \( 2^{22}Rn\lambda_{222}V \) is the radon decay (Bq s\(^{-1}\)) and \( J_{atm} \) is radon atmospheric evasion (Bq s\(^{-1}\)).

Radon atmospheric evasion can be the significant sink of radon in aquatic systems. Radon flux to the atmosphere depends on molecular diffusion generated by concentration gradients and turbulent transfer, which is dependent on physical processes. The radon atmospheric evasion flux (\( J_{atm} \)) was estimated as follows:

\[ J_{atm} = k (C_{w} - \alpha C_{air}) A \]  

(2)

where \( C_{w} \) and \( C_{air} \) are the radon concentrations in water and air, respectively; \( A \) is estuary area (m\(^2\)); \( \alpha \) is the Ostwald solubility coefficient (dimensionless) describing the distribution of radon at equilibrium as the fluid to-gas ratio (0.2 at 20°C); and \( k \) is the piston velocity or the measure of the velocity of gas transfer at the air–water boundary (cm hr\(^{-1}\)). Winds, currents, and depths are usually the drivers of piston velocity in tidal systems (Zappa et al., 2003). Piston velocity (\( k \)) driven by winds and currents were estimated separately using Equations (3) and (4) and their sum was incorporated in Equation (2). Equation (3) was used to calculate piston velocity driven by winds (Hahm et al., 2006):

\[ k_{600wind} = 0.45\mu^{1.6} (Sc / 600)^{-a} \]  

(3)

where \( \mu \) is wind speed (m s\(^{-1}\)); \( Sc \) is the Schmidt number for radon at a given water temperature; and “\( a \)” is a variable power function dependent on wind speeds (\( a = 0.6667 \) for \( \mu < 3.6 \) m s\(^{-1}\), and \( a = 0.5 \) when \( \mu > 3.6 \) m s\(^{-1}\)). The Schmidt number was calculated based on
formulations given by MacIntyre et al. (1995). In order to quantify current-driven evasion, Equation (4) from Borges et al. (2004).

\[ k_{600\text{current}} = 1.719 w^{0.5} D^{-0.5} \]  

where \( k_{600\text{current}} \) is the piston velocity corrected for turbulence driven by currents, \( w \) is the water current (cm s\(^{-1}\)) and \( D \) is water depth (m).

In Equation (1) groundwater discharge rate (\( F_{gw} \)) is the unknown parameter, all other parameters were measured or modelled. During ebb tide, radon-enriched water moves downstream out of the system, therefore results in a radon flux out of the estuary into the ocean. At flood tide, water moves upstream into the system and therefore, results in a radon source to the estuary. Integrating the fluxes over a full tidal cycle resulted in the net export flux that must be accounted for by upstream sources. The mass balance was calculated over 2 tidal cycles (~ 24h) which started from a low tide and ended at low tide. The uncertainty for each term of the radon mass balance was calculated following the basic rules for error propagation.

A salt balance was also calculated to estimate the fresh groundwater discharge into the estuary. Evaporation was neglected and it was assumed that groundwater is the only source of freshwater input to the different sections of the estuary as no visible lateral surface water inputs occur in the area. The freshwater discharge was obtained by multiplying the fraction of freshwater by total discharge at each measuring station for each time interval. These results were integrated over a tidal cycle to obtain net freshwater export rates.

### 2.2.8 Radium mass balance

The concentrations of radium isotopes (\(^{223}\)Ra and \(^{224}\)Ra) were also used to calculate the net flux of groundwater discharging into the estuary. Surface water fluxes were integrated over a 24h tidal cycle following a mass balance approach similar to radon. By integrating two complete tidal cycles, the model assumes steady state for the 24 h integration period. Refer to Peterson et al. (2010) and Gleeson et al. (2013) for further detail on this approach. Parameters of the model consisted of radium groundwater concentration, tidal inputs and outputs, radioactive decay for short-lived radium isotopes, desorption from suspended sediments and groundwater discharge. Equation (5) estimates \(^{223}\)Ra flux in surface water which groundwater inputs are the only source.
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\[ F_{gw}^{223}Ra_{gw} + F_{up}^{223}Ra_{up} + 223Ra_{Desp} = F_{down}^{223}Ra_{down} + 223Ra\lambda V \]  

where \( F_{gw} \) is the groundwater discharge (m\(^3\) s\(^{-1}\)), \( 223Ra_{gw} \) is the groundwater endmember concentration (Bq m\(^{-3}\)), \( F_{up}^{223}Ra_{up} \) is the upstream \( 223Ra \) input flux during flood tide (Bq s\(^{-1}\)), \( 223Ra_{Desp} \) is desorption from suspended sediments (Bq s\(^{-1}\)), \( F_{down}^{223}Ra_{down} \) is the \( 223Ra \) downstream output flux during ebb tides (Bq s\(^{-1}\)), \( 223Ra\lambda V \) is the \( 223Ra \) decay (Bq s\(^{-1}\)) \([ 223Ra = \text{radium concentration}, \lambda = \text{radium decay rate (0.0608·d}^{-1} \text{) and V = volume of water (m}^{3}\text{)} ]\). All the terms in the mass balance were measured or estimated and the equation was solved for groundwater discharge. Considering the negligible contribution of diffusion to radon budgets (shown below) and a series of previous studies demonstrating diffusion is a negligible source of radium isotopes in sites with active SGD (Beck et al. 2007; Beck et al. 2008; Moore, 2000), we neglect diffusion as a source of radium isotopes. A similar mass balance model was used for \( 224Ra \).

Radium is especially useful where subsurface mixing of fresh and saline waters occur, therefore by taking advantage of different concentrations and isotopic ratios in shallow and deep groundwater, we distinguished the shallow saline, deep fresh groundwater and oceanic water by constructing a three end member mixing model using short-lived radium isotopes (Moore, 2003) as follows:

\[ f_{SGW} + f_{DGW} + f_{OW} = 1 \]  

\[ 224Ra_{SGW} f_{SGW} + 224Ra_{DGW} f_{DGW} + 224Ra_{OW} f_{OW} + 224Ra_{Des} = 224Ra_m \]  

Where \( f \) indicates the fraction of the shallow saline groundwater (SGW), deep fresh groundwater (DGW), and ocean water (OW) end-members; \( 224Ra_{SGW} \) is \( 224Ra \) activity in the shallow groundwater end-member; \( 224Ra_{DGW} \) is \( 224Ra \) activity in the deep groundwater end-member; \( 224Ra_{Des} \) is desorption from suspended sediments and \( Ra_m \) is \( 224Ra \) activity measured in the estuary water samples. A similar calculation was done for \( 223Ra \). This model assumes that diffusion is a negligible source of radium isotopes. If diffusion was important, diffusion should have an isotopic ratio similar to shallow groundwater and would artificially increase the contribution of shallow groundwater discharge. The fraction of ocean water was calculated by dividing time-specific salinity measured for each sample from the radium time
series data by the highest salinity assuming that the highest salinity (35.5) observation represented 100% ocean water. Water salinity at the mouth of the creek was 35.5 at high tide and around 7.2 at low tide. The fractions were estimated hourly over two tidal cycles using the above equations and an average was taken for each of the ocean water, shallow and deep groundwater fractions. It was assumed that groundwater was the sole source of radium. Therefore, the shallow and deep groundwater fractions obtained were normalized to 100% groundwater. The normalized fractions for shallow and deep groundwater were 0.35 and 0.65 for $^{223}$Ra, 0.3 and 0.7 for $^{224}$Ra in the rainy season and 0.83 and 0.17 for $^{223}$Ra and 0.91 and 0.09 for $^{224}$Ra in the dry conditions. For calculating the groundwater endmember values we multiplied the saline shallow and fresh deep groundwater fractions by the average $^{223}$Ra and $^{224}$Ra concentration in shallow and deep groundwater samples:

$$^{223}\text{Ra}_{GW \text{end-member}} = (f_{SGW} \times ^{223}\text{Ra}_{SGW}) + (f_{DGW} \times ^{223}\text{Ra}_{DGW})$$

(8)

The total groundwater flux into the estuary was then calculated by dividing the excess radium in the water column obtained through Equation (5) by the estimated radium groundwater endmember using the fractions as follows:

$$^{223}\text{Ra} - \text{derived SGD} = \frac{^{223}\text{Ra}}{^{223}\text{Ra}_{GW \text{end-member}}}$$

(9)

Similar equations were applied to $^{224}$Ra. Each term in the radium mass balance was assigned an uncertainty obtained from the source of that data and propagated following the basic rules for error propagation.

2.3 Results

2.3.1 Hydrologic conditions

Contrasting hydrological conditions occurred during each field campaign. One month prior to the time series measurements in February 2013, the area experienced 502 mm of rain with an additional 110 mm of rainfall in March adding up to a total of 612 mm. The June 2013 time series deployment had base flow conditions with only 5.8 mm of rain 3 days and 51 mm in the month prior to field investigations. As a result, the groundwater level during
March was 100 cm higher than in June. Based on the rainfall events of the area and for simplicity, we describe the first and second field experiments as wet and dry seasons. March had an average surface water temperature of 25.9 ºC compared to 19.4 ºC in June. During the time series experiments in March and June, wind speeds were on average 3.1 and 1.7 m s\(^{-1}\), respectively. Salinity showed a tidal trend at all stations, with the magnitude of change decreasing in the upstream direction (Figure 2.3). Salinity at station 4 was never higher than 5 while other stations experienced temporal changes from brackish (5) to saline (up to 35) over a tidal cycle. Salinity increased rapidly during the start of the flood tide just taking 2.5 hours to reach 35.5 and dropped slowly during ebb tide taking a longer time of 5 hours to reach 7 at the downstream station. The tidal amplitude was 1.2 m in March compared to the 0.8 m in June. The two sampling events were performed at different points in the spring-neap tidal cycle; one was semi-diurnal and the other a mixed semi-diurnal. These differing sampling periods may cause changes in tidally driven SGD and prevent a straightforward interpretation of seasonal differences. During the June experiment, salinity in stations 1, 2 and 3 reached 35 at high tide and decreased to 0.4 in station 3 at low tide (Figure 2.3).
2.3.2 Radon time series

Radon followed a tidal trend increasing at low tide and decreasing at high tide (Figure 2.3). This trend was clearly seen at stations 1, 2 and 3 and with a time lag at station 4. The average radon concentration in stations 1, 2, 3 and 4 were 53±5, 106±7, 126±9 and 144±10 Bq m$^{-3}$, respectively. Radon varied between 0.7±0.5 Bq m$^{-3}$ at high tide at station 1 and 268±13 Bq m$^{-3}$ at low tide at station 2. In the dry season (June), similar trends of radon and salinity to the wet season were observed. The average radon concentration in stations 1, 2 and 3 were 74±5, 133±7 and 174±8 Bq m$^{-3}$, respectively. These values are 1.4, 1.2, and 1.4 fold
higher than the average concentrations observed during the wet season (March) experiment. Radon had an inverse trend with salinity in both seasons and in all stations (Figure 2.3).

2.3.3 Radium isotope time series

Radium samples were collected hourly for 24 hours in March and June 2013 at station 1 at the mouth of the estuary. $^{223}$Ra and $^{224}$Ra activities showed an inverse relationship with estuary water levels (Figure 2.4) indicating input of radium-enriched sources during low tide. Radium isotope concentrations were on average 1.4 and 1.2 fold higher in wet (March) compared to dry (June) for $^{223}$Ra and $^{224}$Ra, respectively. A broader range was seen in radium isotopes in the wet conditions. No simple linear correlation was observed between radium isotopes and salinity (Figure 2.5). Different radium concentrations at the same depth during the ebb and flood tide were found, demonstrating a hysteresis patterns. Radium concentrations were lower in high salinity waters and higher in brackish water.

![Figure 2.4](image_url) Temporal variability of radium isotopes with water level.
Figure 2.5 Activities of $^{223}\text{Ra}$ vs. salinity and depth of estuary water samples for $^{223}\text{Ra}$ in wet and dry seasons. Similar patterns were observed for $^{224}\text{Ra}$. The arrows indicate hysteresis pattern.

2.3.4 Groundwater observations

Groundwater samples were classified in two classes; deep (>5 m), and shallow (<5 m), considering the observed chemical signatures. Average radon in samples collected from shallow bores (459 ± 314 Bq m$^{-3}$, n=17; ± 1 standard deviation) had no significant difference to those measured from deep wells (476 ± 381 Bq m$^{-3}$, n=10). Radon in shallow bores and deep wells ranged between 25 to 1403 Bq m$^{-3}$ in salinities varying from 0.1 to 30.5 (Table 2.1). The average radon concentration in deep and shallow groundwater was 467 ± 346 Bq m$^{-3}$, which was 4.5 fold higher than the average radon (107 ± 90 Bq m$^{-3}$) found in surface
estuarine water. The average radon value in all groundwater samples was used as the radon groundwater endmember for the mass balance.

Average $^{223}\text{Ra}$ and $^{224}\text{Ra}$ activities in shallow saline groundwater samples were 18.5 and 81.2 times higher respectively than those found in deep well samples (Figure 2.6). The $^{226}\text{Ra}$ in the deep groundwater samples was 1.6 times higher than in the shallow groundwater samples, which may be due to the geology of the study site. The average $^{223}\text{Ra}$, $^{224}\text{Ra}$, $^{226}\text{Ra}$ values in shallow samples was $29\pm 5$, $483\pm 74$ and $14\pm 2$ dpm 100L$^{-1}$ respectively. Deep groundwater samples had activities of $1.5\pm 0.2$, $5.9\pm 1.5$ and $23.8\pm 2.8$ dpm 100L$^{-1}$ for $^{223}\text{Ra}$, $^{224}\text{Ra}$, and $^{226}\text{Ra}$ respectively.
Figure 2.6 $^{222}$Rn and $^{223,224}$Ra vs. salinity from deep and shallow groundwater samples.
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and Radium Isotopes

Table 2. 1 Results of groundwater observation.
222Rn

223Ra

224Ra

226Ra

(Bq m-3)

(Bq 100L-1)

(Bq 100L-1)

(Bq 100L-1)

573.8

1.2±0.2

34.5±1

15.2±2.4

0.1

1402.8

0.3±0.1

2.2±0.2

31.2±3.7

4

0.1

365.4

0.7±0.2

1.7±0.1

13.5±2.5

E153.02621

10

0.2

209.3

4.1±0.6

11.6±0.5

16.2±3

S31.00714

E153.02606

18

0.1

247.2

0.2±0.1

0.1±0.1

8/06/13

S31.00714

E153.03242

4

0.1

104.6

0.6±0.1

7.7±0.3

24.5±4

GW 10

8/06/13

S31.02128

E153.02477

6

0.1

135.3

2.3±0.3

15.2±0.4

31.4±3.3

GW 11

8/06/13

S31.02122

E153.02477

21

0.1

867.9

0.3±0.1

1.7±0.2

24.8±3.9

GW 12

9/06/13

S31.30582

E153.03833

2.5

0.2

26.6

1.8±0.4

9.3±0.4

25.8±4.1

GW 13

8/06/13

S31.05657

E153.03668

11.7

0.2

181.2

1.2±0.3

6.1±0.4

19.3±3

GW 14

9/06/13

S31.05353

E153.03702

7.5

0.1

561.2

0.3±0.1

1.7±0.2

28.4±4.1

GW 15

9/06/13

S31.05622

E153.03357

2

0.1

266.4

2.7±0.5

6.9±0.4

25.7±3.7

GW 16s2

10/06/13

S31.04289

E153.03462

2

2.2

605.2

0.4±0.1

1.6±0.1

6.7±1.9

GW

17s2

10/06/13

S31.04290

E153.04290

1.5

1.5

833.8

0.5±0.2

1.9±0.1

GW

18s2

10/06/13

S31.04291

E153.04291

2

0.1

249.8

0.6±0.2

2.6±0.2

9±1.6

GW 19s3

10/06/13

S31.05054

E153.04248

1.5

14.8

469.8

5.5±0.6

11.1±0.4

24.7±2.1

GW

20s3

10/06/13

S31.05059

E153.05066

1.2

0.3

586.5

1.7±0.3

4.2±0.3

11.6±1.7

GW

21s3

10/06/13

S31.05066

E153.04233

1.5

1.8

443.6

2.2±0.3

11.2±0.4

5.6±1.2

GW 22

11/06/13

S31.06817

E153.03395

30

0.1

240.3

0.3±0.1

1.6±0.1

34.9±3.5

GW 23

11/06/13

S31.06834

E153.03387

10.8

0.1

451.3

0.9±0.2

3.2±0.2

37.7±3.1

GW 24

11/06/13

S31.06989

E153.03242

4.5

0.1

158.5

3.6±0.5

8.7±0.3

58.1±3.8

GW 25

11/06/13

S31.09198

E153.01311

10.5

0.1

103.3

0.2±0.1

0.5±0.1

41.8±4.3

GW 26

11/06/13

S31.00847

E153.02598

11.7

0.1

501.2

0.5±0.2

2.2±0.2

39.9±3.6

GW 27

12/06/13

S31.02071

E153.02472

5.5

0.1

416.0

2.3±0.3

15.9±0.4

10.7±2.1

GW28

26/03/13

S31.05761

E153.05642

1

7.5

20.9±4.2

625±47

20.2±6.5

GW29

27/03/13

S31.05759

E153.05642

0.5

7.89

28.9±2.9

363±14.5

17.1±3.4

GW30

27/03/13

S31.05751

E153.05641

2

20.3

34.5±3.1

433±15.3

12.3±1.7

GW31

27/03/13

S31.05748

E153.05641

1

8.4

44±3.6

686±19.4

8.4±2.5

GW32

27/03/13

S31.05745

E153.05641

2

21.5

15.9±2.6

306±18.9

13.6±2.8

Ave.

6.32

5.09

466.8

6.12±2

76.3±4

18.6±3

Max

30.00

30.90

1598.8

44±3.6

686±19.4

58.1±3.1

Min

0.50

0.10

24.8

0.2±0.1

0.1

6.7±1.9

Sample

Depth

Date

Longitude

Latitude

GW 1s1

7/06/13

S31.05745

E153.05642

1.5

30.9

24.8

GW

2s1

7/06/13

S31.05750

E153.05646

1.5

25.7

1598.8

GW

3s1

8/06/13

S31.05756

E153.05648

1.8

17.9

941.3

GW 4

12/06/13

S30.99787

E153.02509

5.5

0.1

GW 5

12/06/13

S30.99986

E153.02757

16

GW 6

12/06/13

S31.00027

E153.03242

GW 7

8/06/13

S31.02943

GW 8

8/06/13

GW 9

ID

(m)

Salinity

Note that s1, s2 and s3 indicate samples from the vicinity of station 1, 2 and 3, respectively.

28


2.3.5 Mass balance models

A radon mass balance was calculated for the March and June time series deployments. Since we did not have data for station 4 in June, the mass balance was solved using three stations in the dry season. Diffusion from sediments and radioactive decay were the smallest radon source and sink respectively during both seasons (Table 2.2). Wind and current-driven evasion had similar contribution to radon loss from the system in both of the field experiments. The sediment core experiments revealed that molecular diffusion fluxes were very low with diffusion rates of 2.4±0.8 Bq m⁻² d⁻¹. These fluxes were then extrapolated to the whole estuary area (116,160 m²) and accounted for less than 2% of all radon sources. The decay of ²²⁶Ra was a small source of radon as the average ²²⁶Ra in surface water was <1% of the average radon. The main loss term in the radon mass balance was water-borne exports with values an order of a magnitude higher than other terms (Table 2.2).

### Table 2.2 Calculated results from the radon mass balance model over a full tidal cycle during wet (March) and dry (June) seasons in Korogoro estuary (all values in units of Bq s⁻¹ integrated over a full tidal cycle).

<table>
<thead>
<tr>
<th>Sampling season</th>
<th>Box</th>
<th>Upstream inputs (Bq s⁻¹)</th>
<th>Diffusion from sediment (Bq s⁻¹)</th>
<th>Rn decay (Bq s⁻¹)</th>
<th>Wind evasion (Bq s⁻¹)</th>
<th>Current evasion (Bq s⁻¹)</th>
<th>Downstream outputs (Bq s⁻¹)</th>
<th>Missing radon (groundwater) (Bq s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet - March</td>
<td>A</td>
<td>200.6±23.6</td>
<td>3.2±1.1</td>
<td>6.6±1.2</td>
<td>22.2±3.2</td>
<td>29.3±6</td>
<td>219.4±29.6</td>
<td>73.9±38.5</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>188.6±24.9</td>
<td>3.2±1.1</td>
<td>4.3±1</td>
<td>17.7±2.1</td>
<td>6.1±0.1</td>
<td>200.6±23.6</td>
<td>37.1±34.3</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>213.3±25.9</td>
<td>3.2±1.1</td>
<td>4.0±0.6</td>
<td>12.5±1.9</td>
<td>12.7±3.4</td>
<td>188.6±24.9</td>
<td>1.6±36.1</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>3.2±1.1</td>
<td>7.9±2.4</td>
<td>17.9±3.5</td>
<td>16.6±5.1</td>
<td>213.3±25.9</td>
<td>252.2±93.5</td>
<td></td>
</tr>
<tr>
<td>Dry - June</td>
<td>A</td>
<td>67.5±7.5</td>
<td>3.2±1.1</td>
<td>12.1±2.4</td>
<td>21.8±4.4</td>
<td>29.6±5.9</td>
<td>76.7±10.4</td>
<td>69.5±14.8</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>74.4±10.1</td>
<td>3.2±1.1</td>
<td>7.1±1.8</td>
<td>17.4±3.4</td>
<td>16.4±3.2</td>
<td>67.5±7.5</td>
<td>30.8±13.5</td>
</tr>
<tr>
<td></td>
<td>C+D</td>
<td>3.2±1.1</td>
<td>9.5±1.8</td>
<td>20.8±5.7</td>
<td>17.8±4.9</td>
<td>74.4±10.1</td>
<td>119.3±35.8</td>
<td></td>
</tr>
</tbody>
</table>

The missing radon fluxes were assumed to be groundwater discharge, therefore by dividing the missing radon flux from all the boxes (Table 2.2), by the groundwater endmember concentration, volumetric groundwater discharge rates of 0.78±0.18 m³ s⁻¹ for wet (March) and 0.47±0.17 m³ s⁻¹ for dry (June) were calculated (Table 2.3). Considering the estuary area of 116,160 m², estuarine-averaged groundwater fluxes were estimated to be
56.1±12.9 cm d$^{-1}$ for the wet and 34.95±12.5 cm d$^{-1}$ for the dry season. The highest input of groundwater occurred in box D in the wet and box C+D in dry season (Table 2.3). Box A had a similar groundwater discharge rate to Box B in both seasons, while Box C located at the upstream of the estuary had a lowest groundwater discharge rate of 0.05 ± 0.04 m$^3$s$^{-1}$ (25 ± 20 cm d$^{-1}$) in the wet season. Cumulative (i.e., the sum of all boxes) groundwater inputs were considered when estimating the percentage of groundwater contribution to the total fresh surface water exports. The radon-derived groundwater discharge rate (a sum of shallow and deep SGD) represented 22.3% of the total net fresh surface water export from the estuary to the ocean (explained below) in wet conditions and 16.7% in the dry season.

Table 2.3 Water fluxes entering different parts of the estuary during seasons with contrasting rainfall events with a calculated groundwater in surface water percentage.

<table>
<thead>
<tr>
<th>Sampling season</th>
<th>Box</th>
<th>Upstream inputs (m$^3$s$^{-1}$)</th>
<th>Downstream outputs (m$^3$s$^{-1}$)</th>
<th>Groundwater Flux (m$^3$s$^{-1}$)</th>
<th>Contribution of GW flux to downstream freshwater exports (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet season (March)</td>
<td>A</td>
<td>1.19</td>
<td>1.27</td>
<td>0.17±0.08</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.15</td>
<td>1.19</td>
<td>0.08±0.07</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1.12</td>
<td>1.15</td>
<td>0.05±0.04</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>1.12</td>
<td>0.48±0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td>0.78±0.18</td>
<td></td>
<td>22.3</td>
</tr>
<tr>
<td>Dry season (June)</td>
<td>A</td>
<td>1.07</td>
<td>1.11</td>
<td>0.16±0.04</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.01</td>
<td>1.07</td>
<td>0.07±0.03</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>C + D</td>
<td></td>
<td>1.01</td>
<td>0.24±0.05</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td>0.47±0.17</td>
<td></td>
<td>16.7</td>
</tr>
</tbody>
</table>

The salt mass balance indicated that 1.12 m$^3$s$^{-1}$ of freshwater enters the estuary from station 4 and 1.27 m$^3$s$^{-1}$ freshwater leaves station 1 averaged over a 24 h time scale, giving an estimated total groundwater discharge rate from boxes A, B and C of 0.15 m$^3$s$^{-1}$ or 13.7 cm d$^{-1}$, in the wet season (Table 2.3). This does not include the upstream of station 4 (box D). This groundwater discharge rate is 1.6 times smaller than the radon mass balance estimation excluding the upstream of station 4 inputs (only accounting for boxes A, B and C). This is reasonable since radon is detecting both fresh and saline groundwater while the salt mass balance is accounting for fresh groundwater only. The salt balance revealed that the highest area-specific groundwater flow, was entering the estuary from box B (19.6 cm d$^{-1}$ or 0.04 m$^3$
s\(^{-1}\) over the box area), although volumetrically box A showed higher input rates (13.1 cm \(d^{-1}\) or 0.08 m\(^3\) s\(^{-1}\) over the box area).

The upstream and downstream flows were the key terms in the radium mass balance model. It was also found that desorption from suspended sediments was a negligible source (<1% of total exports) of radium to the estuary (Table 2.4). Decay rates were a small component of the model. Results from the radium mass balance showed a net export of both short lived radium isotopes which indicates groundwater discharging into the estuary. As summarized in Table 2.5, groundwater discharge rates were 0.91±0.25 and 1.18±0.65 m\(^3\) s\(^{-1}\) (or 65.2±18.2 and 84.4±48.7 cm \(d^{-1}\)) in the wet season based on the \(^{223}\)Ra and \(^{224}\)Ra respectively (Table 2.5). In the dry season discharge rates were 0.21±0.09 m\(^3\) s\(^{-1}\) (18.8±5.6 cm \(d^{-1}\)) and 0.24±0.1 m\(^3\) s\(^{-1}\) (20.4±6.7 cm \(d^{-1}\)) calculated by the \(^{223}\)Ra and \(^{224}\)Ra mass balance, respectively. It was found that surface water discharge over a 24h time scale was 1.5 fold higher in the wet compared to dry conditions, while groundwater discharge rates calculated from \(^{223}\)Ra and \(^{224}\)Ra isotopes were 4.2 and 4.8 fold higher in the wet compared to the dry season.

**Table 2.4** \(^{223}\)Ra and \(^{224}\)Ra mass balance parameters used to calculate the total groundwater flux into the estuary in the wet (March) and dry (June) seasons.

<table>
<thead>
<tr>
<th></th>
<th>Wet</th>
<th>Dry</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Radium-223</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{223})Ra(_{SGW}) (Bq m(^{-3}))</td>
<td>4.81±0.8</td>
<td>4.81±0.8</td>
</tr>
<tr>
<td>(^{223})Ra(_{DGW}) (Bq m(^{-3}))</td>
<td>0.25±0.05</td>
<td>0.25±0.05</td>
</tr>
<tr>
<td>Desorption (Bq s(^{-1}))</td>
<td>0.01±0.02</td>
<td>0.01±0.02</td>
</tr>
<tr>
<td>Net export (Bq s(^{-1}))</td>
<td>1.68±0.4</td>
<td>0.51±0.06</td>
</tr>
<tr>
<td>Decay (Bq s(^{-1}))</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Radium-224</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{224})Ra(_{SGW}) (Bq m(^{-3}))</td>
<td>80.43±12.3</td>
<td>80.43±12.3</td>
</tr>
<tr>
<td>(^{224})Ra(_{DGW}) (Bq m(^{-3}))</td>
<td>0.99±0.3</td>
<td>0.99±0.3</td>
</tr>
<tr>
<td>Desorption (Bq s(^{-1}))</td>
<td>0.01±0.02</td>
<td>0.01±0.02</td>
</tr>
<tr>
<td>Net export (Bq s(^{-1}))</td>
<td>29.1±4.8</td>
<td>9.43±0.46</td>
</tr>
<tr>
<td>Decay (Bq s(^{-1}))</td>
<td>0.52</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Table 2.5 Groundwater discharge rates (m$^3$ s$^{-1}$) from radon and radium isotope mass balance models in wet and dry seasons.

<table>
<thead>
<tr>
<th>Approach</th>
<th>Wet season</th>
<th>Dry season</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shallow</td>
<td>Deep</td>
</tr>
<tr>
<td>$^{222}$Rn (m$^3$ s$^{-1}$)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>$^{223}$Ra (m$^3$ s$^{-1}$)</td>
<td>0.32±0.11</td>
<td>0.59±0.16</td>
</tr>
<tr>
<td>$^{224}$Ra (m$^3$ s$^{-1}$)</td>
<td>0.35±0.1</td>
<td>0.83±0.47</td>
</tr>
</tbody>
</table>

n.d. = not determined.

2.4 Discussion

2.4.1 Radon and radium mass balance model uncertainties

The key strength of this study lies in coupling synchronized high temporal resolution radon data using multiple time series stations, and the use of multiple radionuclide tracers. Most previous studies on SGD tracers have focused on temporal (Gleeson et al., 2013) or spatial (Su et al., 2014) aspects or even temporal and spatial (Peterson et al., 2008a; Maher et al., 2015) but not necessarily at the same time. Some have combined the use of radionuclide tracers such as $^{222}$Rn and Ra isotopes (Rodellas et al., 2012; Baudron et al., 2015). However, previous studies have used up to two-time series stations as the model domain boundaries (Santos et al., 2014; Atkins et al., 2013). Here, we performed simultaneous multiple radon high resolution time series measurements combined with high temporal radium sampling in an estuarine system. Utilization of natural tracers and mass balance approaches in SGD studies has always been challenged with uncertainties in quantifying groundwater discharge rates (Knee and Paytan, 2011). Our extensive sampling strategy may allow for a better description of the major terms of the mass balance and reduce uncertainties in the estimated groundwater discharge rate.

We accounted for analytical uncertainties in radon measurements, current velocities, atmospheric evasion and the groundwater endmember. Also, uncertainties associated with determining the point of entry of groundwater into the system were investigated. Uncertainties related to radium isotopes desorption from suspended sediments and molecular diffusion from sediments were considered negligible components of the mass balance and are not explored further here.
In the estuary investigated, tidal exports were by far the dominant source and sink of radon due to tidal inputs and outputs being an order of magnitude higher than other terms. The average analytical uncertainty for each 30 min radon counting cycle was usually about 5%, with analytical uncertainties as high as 70% when radon concentrations were the lowest at high tide. Readings from the current meter were assigned an uncertainty of 2% obtained from the manufacturer. Therefore, to account for a maximum uncertainty, an overall analytical uncertainty of 10% was assigned to the tidal flow term.

Radon evasion driven by currents and winds were separately accounted for and were found to be a minor (~15%) term of radon losses in each box. However, because surface water radon input/output were within the error of each other (except for Box B in June), surface flows were in near balance. Thus, the real control on groundwater discharge rates may be evasion rates as the balance of losses is closely associated with evasion fluxes. Evasion is enhanced by current and wind driven water turbulence, which is important in shallow estuarine systems (Zappa et al., 2003, Borges et al., 2004). A model which calculates piston velocity as a function of water depth, current and wind speed was employed in our case to account for the dominant sources of water turbulence in estuarine systems (Borges et al., 2004). This model may produce a maximal uncertainty due to the propagation of errors associated with the use of three terms (wind speed, depth and current velocity) as opposed to using wind speeds only as in most previous radon studies (Santos and Eyre, 2011). An uncertainty of 1% was allocated to the measured water depth based on the instrument specifications and 10% to the measured wind speed measurements based on the wind speed data source. In addition, the piston velocity alone was related to a 10% uncertainty based on propagation of errors related to data used to derive the piston velocity. Combining these potential issues generates an average uncertainty of 18% for the evasion term alone.

Previous studies have used one station for calculating evasion rates and up scaling to the whole estuary area (Peterson et al., 2010). They applied a maximum and minimum scenario by assuming that all groundwater entered surface waters at the most upstream point which yields a maximum groundwater discharge rate or all groundwater entered surface waters exactly at the observation site to gain minimum groundwater discharge rate. Santos et al. (2014) used two stations at the boundaries of an estuary to avoid those scenarios. Using multiple measuring stations may be an adequate way to address the large heterogeneity of coastal waters. However, in our case there may be limitations associated with our evasion fluxes due to the formulation applied here for our small and narrow fetch limited water body.
Another limitation may be related to wind speeds at each site which may be quite different from that measured 15 km away due to the dunes and vegetation affecting the micrometeorology of the site. Most previous studies only consider wind driven evasion in the mass balance (Burnett and Dulaiova, 2006, Smitha and Swarzenski, 2012, Gwak et al., 2013). If the current driven evasions in this study were neglected, the final groundwater discharge rates for the wet and dry season would decrease by 18% and 21%, respectively. Winds had a similar effect to currents on radon evasion. This demonstrates that not accounting for current driven evasion in the radon mass balance approach will underestimate groundwater discharge rates in shallow tidal estuarine systems.

In both the radon and radium mass balance models, the most important source of uncertainty is often in allocating an endmember value to groundwater (Dulaiova et al., 2008). The concentration of radon and radium in groundwater can vary widely over small spatial scales (Schmidt et al., 2010, Smith et al., 2008). Previous studies have collected from 5 to more than 40 groundwater samples for endmember determination (Peterson et al., 2008a, Su et al., 2014, de Weys et al., 2011). It has been suggested that increasing the number of samples may decrease uncertainties and provide a more reasonable estimate of the groundwater endmember (Makings et al., 2014, Santos et al., 2014, Charette, 2007). What is the ideal number of samples? This was investigated by calculating the standard error of average radon concentrations for a sample size of 2 and randomly adding more samples until all 27 samples were included (Figure 2.7). We use radon to illustrate the importance of reasonable sample size because concentrations did not vary significantly in the shallow saline and deep fresh groundwaters. Figure 2.7 shows how increasing the sample size reduces the standard error. Here, the standard error of 87% using only 5 samples was decreased to 20% using all the radon samples (n=27). A sample size of about 12 would be sufficient as the standard error starts to stabilize beyond this amount of samples. Accordingly, an uncertainty of 20% for the radon endmember term was assumed in the last part of the mass balance calculation, where radon fluxes are converted to water fluxes (uncertainties refer to the standard error of all samples reported in Table 2.1). However, the conclusion made here based on radon may not be extrapolated for short-lived Ra isotopes. As illustrated in Figure 2.7, if several groundwater samples with different concentrations are collected and there is large variability, the uncertainty will still be large. This may be particularly important for radium groundwater sampling where salinity plays an important role (Swarzenski et al.
Moreover, the number of required samples may be site specific and vary based on the characteristic of the site.

Figure 2.7 Standard error for average radon, $^{223}$Ra and $^{224}$Ra concentration using different sample sizes. Radon and radium samples (fresh and saline) were randomized. The jumps in radium concentrations are related to a saline groundwater sample. We highlight that taking average radium concentrations for all samples is not realistic because the samples can be easily separated as fresh (low concentration) and saline (high concentration).
2.4.2 The importance of spatially distributed time series stations

Calculating uncertainty in tracer studies can be challenging. Table 2.6 shows reported uncertainties from other studies using a radon mass balance approach to quantify groundwater discharge. Uncertainties estimated in studies which use two measuring stations are lower than when using a single time series station (Peterson et al., 2010, Atkins et al., 2013, Santos et al., 2014). This may be related to the similar experimental strategy aimed at closing gaps in the mass balance approach. However, conducting surveys in lakes and lagoons produces a similar range of uncertainty of about 70% when applying the radon mass balance approach (Su et al., 2014, Dimova et al., 2013, Gwak et al., 2013). Although one station may be enough for determining the SGD rates using radium in coastal waters (Garcia-Orellana et al., 2010), relying only on one station in estuaries when using radon provided the highest uncertainty among different studies (Burnett et al., 2008, Peterson et al., 2008a, Smitha and Swarzenskib, 2012). On the other hand, the estimated uncertainty in this work (23%) is lower than those utilizing two stations (27 – 45%), highlighting the importance of combining spatially distributed time series stations. The overall uncertainty of the groundwater discharge rate from the radon mass balance in the rainy season (March) using four stations was 23% in total, with the SGD rate ranging between 43.2 – 69.1 cm d⁻¹. If we follow Peterson et al. (2008a) minimum and maximum scenario approach relying on one station for calculating groundwater discharge, the estimated rate would vary between 35 ± 8 – 51 ± 12 cm d⁻¹ with an uncertainty of >41%. Also the maximum estimate (63.2 cm d⁻¹) would be 10% lower than the maximum estimate using the four station approach. Therefore, using only one station may underestimate the total groundwater discharge as well as increase the overall uncertainty.
Table 2.6 Uncertainties from other studies using a radon mass balance approach to calculate groundwater discharge.

<table>
<thead>
<tr>
<th>Location</th>
<th>Uncertainty</th>
<th>Approach</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hat Head, NSW, Australia</td>
<td>23%</td>
<td>TS * 4</td>
<td>This study</td>
</tr>
<tr>
<td>Hat Head, NSW, Australia</td>
<td>40%</td>
<td>TS * 1 / Min – Max scenario</td>
<td>This study</td>
</tr>
<tr>
<td>Little lagoon, Alabama, USA</td>
<td>70%</td>
<td>Survey</td>
<td>Su et al. (2014)</td>
</tr>
<tr>
<td>Waikareao lagoon, New Zealand</td>
<td>27%</td>
<td>TS * 2</td>
<td>Santos et al. (2014)</td>
</tr>
<tr>
<td>Te Puna lagoon, New Zealand</td>
<td>45%</td>
<td>TS * 2</td>
<td></td>
</tr>
<tr>
<td>Lake Hunter, Florida, USA</td>
<td>66.5%</td>
<td>Survey</td>
<td>Dimova et al. (2013)</td>
</tr>
<tr>
<td>Gwang watershed, South-eastern Korea</td>
<td>67%</td>
<td>Survey</td>
<td>Gwak et al., (2013)</td>
</tr>
<tr>
<td>Muri Lagoon, Cook Island, central south pacific</td>
<td>75%</td>
<td>3 approaches</td>
<td>Tait et al. (2013)</td>
</tr>
<tr>
<td>Tidal creek, Richmond river, NSW, Australia</td>
<td>27%</td>
<td>TS * 2</td>
<td>Atkins et al. (2013)</td>
</tr>
<tr>
<td>Tampa Bay, Florida, USA</td>
<td>71%</td>
<td>Survey</td>
<td>Smith and Swarzenski (2012)</td>
</tr>
<tr>
<td>Sebastian River Estuary, Florida, USA</td>
<td>27%</td>
<td>TS * 2 / Min - Max scenario</td>
<td>Peterson et al. (2010)</td>
</tr>
<tr>
<td>Yellow River delta, China</td>
<td>120%</td>
<td>TS * 1</td>
<td>Peterson et al. (2008)</td>
</tr>
<tr>
<td>Estuary, Ubatuba, Brazil</td>
<td>93%</td>
<td>TS * 1</td>
<td>Burnett et al. (2008)</td>
</tr>
</tbody>
</table>

TS = time series.

Groundwater is spatially variable and thus it is difficult to assess the exact area where discharge occurs. Deploying multiple stations to break down the estuary into smaller segments allowed the calculation of more reasonable groundwater discharge rates and enabled the major discharge area to be narrowed down to within smaller segments of the estuary. In our case while the estimated aerial groundwater discharge rates were within the wide range of previous studies in estuaries and intertidal systems (Moore, 2010, Burnett et al., 2006), we were able to detect the highest groundwater discharge rates within a well-defined small area of the estuary (i.e. box D). Knee and Jordan (2013) have also reported similar results which indicate more groundwater influx occurs in the upstream part of an estuary. Box B had the second area-specific groundwater flow (Table 2.3). This area had sand dunes along the estuary where effluent disposal is thought to artificially raise the local water table as it is discharged directly in the sand dunes (Figure 2.1) (Ruprecht and Timms, 2010). Box A discharge rates were slightly lower. Most of the surface sediments in box A were sandy and as the estuary is tidal, water infiltrates into beach sediments at high tide and recirculates back out to the estuary at low tide. Thus, most of the groundwater discharging from box A is likely recirculated seawater as implied from the radium mixing model (see below). Moreover, groundwater discharge rates did not change significantly in wet and dry
seasons in box A, indicating tidal pumping is a dominant source of radon in that section. Box C had the lowest groundwater discharge rate. The estuary has a small low lying catchment and therefore, does not have high amounts of fresh surface water discharge from the catchment (Acworth et al., 2007), thus groundwater discharging upstream of station 4 may be related to higher groundwater table in that area which builds up a hydraulic head and facilitates the groundwater discharge into the estuary. Previous studies that relied only on a single station at the most downstream point of the area of interest, cannot resolve the exact location of groundwater discharge (Burnett et al., 2010; de Weys et al., 2011; Peterson et al., 2010). In this study, spatially distributed time series stations allowed for additional insights on groundwater discharge points by providing quantitative estimates of groundwater entering different areas of the estuary.

2.4.3 Tracer dynamics over tidal time scales

An initial perception of the radon and radium data plotted against salinity (Figures 2.5 and 2.8) implies a linear relationship which has also been reported by previous studies (Charette et al., 2013, Peterson et al., 2009b, Su et al., 2014). However, by grouping the data in ebb and flood tide periods as illustrated in Figure 2.5, the linear relationship becomes inconspicuous and a hysteresis pattern emerges making the interpretation more complex. The hysteresis is likely related to a quick seawater intrusion (i.e., 2 hours for brackish water to reach station 4 approximately 4 km upstream) and delayed drainage (~ 9 hours) to flush out the estuary during the ebb tide. As illustrated in Figure 2.8 salinity starts to decrease at ebb tide while the radon concentration remains low and constant. This indicates that fresh surface water (which is low in radon and radium) is initially transported from the nearby wetlands into the estuary until the estuary water level drops below the groundwater level, and groundwater seeps into the estuary, quickly increasing tracer concentrations. This hysteresis illustrates the importance of performing high temporal resolution time series (24 h) sampling to resolve a mass balance model. Hysteresis patterns have been previously observed in the response of surface waters to rain events (Rudorff et al., 2014; Moravcová et al., 2013; Seeger et al., 2004). Overall, the radon concentration pattern suggests that the lateral advection of groundwater into the estuary is not steady-state over time scales of hours but rather oscillates over a tidal cycle. Therefore, integrating observations for at least an entire tidal cycle is required to estimate groundwater discharge under those conditions.
Figure 2.8 Hysteresis patterns emerging from the radon verses salinity and depth data collected at station 1 in wet and dry seasons. Similar patterns were observed at other stations. The arrows indicate hysteresis pattern.

2.4.4 Groundwater source: deep fresh vs shallow saline

Groundwater with different sources may have different concentrations of solutes. Therefore, in order to investigate the influence of groundwater discharge each source has to be assessed according to its chemical signature (Moore, 2003). Fresh terrestrial groundwater and recirculated seawater may release radon and radium isotopes to surface waters. Radon concentrations were similar in saline shallow and fresh deep groundwaters (Figure 2.6). Therefore, it is not possible to differentiate these sources using radon. Radium isotopes, however, had contrasting concentrations in shallow and deep groundwater and oceanic water allowing the use of a three end member mixing model (Moore, 2003).

Table 2.4 presents the radium isotope mass balance parameters used to estimate groundwater discharge into the estuary using equations (5) to (11). The models were applied
for both of the field experiments. The average $f_{SGW}$, $f_{DGW}$, and $f_{OW}$ in the wet period were 0.10, 0.19, and 0.71, for $^{233}$Ra and 0.09, 0.21 and 0.70 for $^{224}$Ra, respectively. In the dry season these values changed to 0.32, 0.07 and 0.61 for $^{223}$Ra and 0.36, 0.04 and 0.61 for $^{224}$Ra, respectively (Figure 2.9). While negative values are not possible for fractions (Moore, 2003), small negative values were encountered for $f_{DGW}$ at high tide in both wet and dry seasons calculations. This is likely related to uncertainties in endmembers, particularly when groundwater concentrations are small (as is the case at high tide). Lamontagne et al. (2008), also obtained negative fractions when applying mixing models to calculate groundwater discharge in South Australian coastal waters.

The fractions reveal that during the wet field campaign, the contribution of deep fresh groundwater was greater than shallow saline groundwater. The opposite occurred during the dry campaign, when shallow groundwater discharge was more important than deep fresh groundwater. Overall, an average of the fractions from the wet and dry conditions indicates that shallow saline groundwater discharge is dominant in the estuary. An explanation for this is that in the March field experiment, groundwater levels rise and the estuary behaves as a gaining stream. At the same time, tidal pumping releases shallow saline groundwater in to the estuary. In June, groundwater levels were 100 cm lower than in March (Annual Groundwater Monitoring Program report, 2013), and tidal pumping was the dominant source of groundwater discharge making the shallow saline groundwater contribution much higher than deep fresh groundwater.
Figure 2.9 Results of the three-endmember mixing model giving the fractions of shallow groundwater (SGW), deep groundwater (DGW) and ocean water (OW) end-members in the estuary surface water obtained from 223Ra and 224Ra in the wet season.

The total groundwater flow calculated using the $^{223}$Ra and $^{224}$Ra mass balance approach was $0.91 \pm 0.25$ and $1.18 \pm 0.65 \text{ m}^3\text{s}^{-1}$, respectively in the period with higher antecedent rainfall. A comparison between the radon and radium tracers illustrates that these rates are within the uncertainties of the radon-derived groundwater discharge ($0.77 \pm 0.17 \text{ m}^3\text{s}^{-1}$) in the same period. However, since radon-based estimates likely represent the total SGD (mixture of fresh and saline) and Ra seems to account for saline SGD only, one would expect Rn-based estimates to be the highest. If we had only used the shallow saline groundwater samples for the end-member in the radon and radium models, radon SGD estimates would be about the same, while radium estimates would be drastically lower (due to high concentrations of radium in shallow saline groundwater samples). Total groundwater discharge estimated from the $^{223}$Ra and $^{224}$Ra calculations in the low rainfall season were $0.21 \pm 0.08$ and $0.24 \pm 0.11 \text{ m}^3\text{s}^{-1}$. These rates however, are lower than the radon-derived calculated groundwater discharge in the dry season ($0.47 \pm 0.17 \text{ cm d}^{-1}$). This may be due to
the endmember value relying much more on the shallow groundwater compared to the fresher deep groundwater. The concentration of $^{233}\text{Ra}$ and $^{224}\text{Ra}$ were about 20 and 70 fold higher in the shallow groundwater, respectively (Figure 2.6). When dividing the unaccounted for radium flux by the higher endmember radium concentration the result is an overall reduction in the estimated groundwater discharge rate in dry season. However, this comparison demonstrates that radon and radium isotopes can provide complementary information.

Moore (2003) highlights the importance of defining an appropriate radium endmember to generate reasonable estimates. Previous studies using mixing models obtained different results based on the endmember values. Moore (2003) pointed out that the model used in Apalachee Bay, northeastern Gulf of Mexico, USA, is sensitive to the endmember and that the overall results of groundwater discharge could change by using different endmembers. In the Gulf of St. Vincent (Adelaide, Australia) a mixing model could not unambiguously determine the proportion of groundwater discharging from the regional aquifer or recirculated seawater (Lamontagne et al., 2008). In another study, mixing models revealed that most of the groundwater discharge was from deep groundwater compared to shallow in a lagoon in Alabama, USA (Su et al., 2014).

Previous studies used average tracer concentration in groundwater samples to determine the endmember (Gleeson et al., 2013, Makings et al., 2014). In order to investigate how the model changes due to endmember selection, we applied the radium mass balance model using the average shallow and deep groundwater radium concentration without the fractions as the endmember. This decreased the final discharge rates by 25% and 38% for $^{223}\text{Ra}$ and $^{224}\text{Ra}$ in the wet season. In the dry season groundwater discharge rates decreased by 29% and 36% for $^{223}\text{Ra}$ and $^{224}\text{Ra}$, respectively. This shows that not assigning the correct fraction of each groundwater source results in a decrease up to 32% of the overall estimated SGD value. Ignoring the different contributions of groundwater makes shallow groundwater samples with higher concentrations disproportionally increase the endmember value. Thus, we suggest assigning the fraction of each source of groundwater to calculate the endmember value as described above. If the deep groundwater samples were excluded and only the average shallow groundwater samples were used as an extreme high endmember value, the total groundwater discharge rates for the wet season would decrease by 61% and 68% for $^{223}\text{Ra}$ and $^{224}\text{Ra}$, respectively. In the dry season, the rates would decrease by 47% and 50% for $^{223}\text{Ra}$ and $^{224}\text{Ra}$. This significant change in the groundwater discharge value shows the
importance of collecting samples from deep fresh and shallow saline groundwater and following a comprehensive sampling strategy to determine the endmember value.

When plotting the surface and groundwater $^{223}\text{Ra}$ against $^{224}\text{Ra}$ with the average activity ratio of deep and shallow groundwater as endmembers (Figure 2.10), it appears that the major source of groundwater to the estuary is from shallow saline groundwaters. Therefore, based on Figure 2.10 another scenario can be investigated where it is assumed that 100% of the radium is coming from shallow saline groundwater whereas the radon is indicating shallow and deep groundwaters. Thus, the difference between radon and radium should result in deep groundwater fluxes. Groundwater discharge (shallow) calculated from this assumption and obtained from $^{223}\text{Ra}$ and $^{224}\text{Ra}$ were 43% and 46% of the total radon derived-SGD in the wet season, respectively. In the dry season, this was 15% and 18% lower than the total radon derived-SGD from $^{223}\text{Ra}$ and $^{224}\text{Ra}$ alone, further supporting the suggestion that deep groundwater dominates discharge during the wet season (~55%), while shallow groundwater contributes ~45% of the total groundwater discharge during the dry. This independent approach gives confidence in the differentiation of deep and shallow groundwater obtained from the endmember fraction approach (equations 9 and 10).
Figure 2.10 Estuary water and groundwater $^{224}$Ra plotted against $^{223}$Ra. The lines show the average $\pm$ standard error of activity ratios in deep and shallow groundwater. The numbers refer to the slope of lines.

2.5 Conclusions

We investigated groundwater discharge into a tidal estuary using multiple radon time series stations and radium isotopes sampled from a single station. We built on previous studies by showing how spatially distributed radon time series stations may provide greater insight into the location of groundwater discharge areas while concurrently reducing uncertainty in groundwater discharge rate estimates. A comparison with previous studies revealed that our extensive, labour intensive radon sampling strategy provides a relatively low propagated uncertainty (23%). We demonstrate that in tidal estuaries, natural geochemical traces may not follow a simple linear relationship with salinity but rather
hysteresis patterns may be observable in the data. The observed hysteresis highlights the need for sampling approaches that can cover both ebb and flood tides, along with an adequate sampling frequency.

A three end member mixing model was constructed to determine the fractions contributed by shallow saline and deep fresh groundwater to the estuary. The mixing model revealed contrasting results for deep vs. fresh groundwater contribution in seasons with contrasting rainfall events. In the wet season, deep fresh groundwater discharging into the estuary contributed 65% compared to the shallow saline groundwater (35%). In contrast, during dry conditions when the groundwater table was a meter lower than in the wet season, a large contribution was estimated for shallow groundwater (80%). The total groundwater (shallow + deep) flux estimated from radium isotopes was within the range estimated from the radon derived mass balance model.
Chapter 3

Groundwater discharge as a source of dissolved carbon and greenhouse gases in a subtropical estuary

Chapter 3 | Groundwater discharge as a source of dissolved carbon and greenhouse gases in a subtropical estuary

Abstract

Groundwater may be highly enriched in dissolved carbon species, but its role as a source of carbon to coastal waters is still poorly constrained. Exports of deep and shallow groundwater-derived dissolved carbon species from a small subtropical estuary (Korogoro Creek, Australia, latitude -31.04781°, longitude 153.06492°) were quantified using a radium isotope mass balance model (233Ra and 224Ra, natural groundwater tracers) under two hydrological conditions. In addition, air-water exchange of carbon dioxide and methane in the estuary was estimated. The highest carbon inputs to the estuary were from deep fresh groundwater in the wet season. Most of the dissolved carbon delivered by groundwater and exported from the estuary to the coastal ocean was in the form of dissolved inorganic carbon (DIC; 687 mmol m⁻² estuary d⁻¹; 20 mmol m⁻² catchment d⁻¹, respectively), with a large export of alkalinity (23 mmol m⁻² catchment d⁻¹). Average water to air flux of CO₂ (869 mmol m⁻² d⁻¹) and CH₄ (26 mmol m⁻² d⁻¹) were 5 and 43 fold higher, respectively, than the average global evasion in estuaries due to the large input of CO₂ and CH₄ enriched groundwater. The groundwater discharge contribution to carbon exports from the estuary for DIC, dissolved organic carbon (DOC), alkalinity, CO₂ and CH₄ was 22%, 41%, 3%, 75% and 100%, respectively. The results show that CO₂ and CH₄ evasion rates from small subtropical estuaries surrounded by wetlands can be extremely high, and that groundwater discharge had a major role in carbon export and evasion from the estuary and therefore should be accounted for in coastal carbon budgets.

Keywords: Submarine groundwater discharge, surface water-groundwater interaction, Carbon dioxide, methane, permeable sediments, radon, cavity ring down spectrometry, mangrove, greenhouse gases.
3.1 Introduction

Estuarine ecosystems provide a major pathway for carbon to travel across the land–ocean interface and are considered an important component of the global carbon cycle (Rodríguez-Murillo et al. 2015; Seitzinger et al. 2005). Estuarine carbon input and transformation processes include material exchange with surrounding environments (Hans et al. 2011) (in particular coastal wetlands (Cai 2011)), high rates of primary productivity and respiration (Bianchi 2007), benthic-pelagic coupling (Maher and Eyre 2010), freshwater inputs (Dixon et al. 2014), atmospheric exchange (Borges and Abril 2011) and groundwater discharge (Liu et al. 2014). Of these processes, groundwater exchange is probably the most poorly resolved and has received little attention until recently.

Groundwater discharge/porewater exchange has been suggested to influence carbon cycling in estuarine environments (Santos et al. 2012a; Faber et al. 2014; Wang et al. 2015). Groundwater inputs to coastal waters may be volumetrically small when compared to surface water inputs, however, due to the high concentrations of dissolved constituents, groundwater can be a major pathway for dissolved material exports between terrestrial and coastal systems (Burnett et al. 2006; Maher et al. 2013a; Liu et al. 2014). Submarine groundwater discharge (SGD) is defined as the exchange of groundwater between land and ocean regardless of its composition and scale and may be fresh terrestrial, recirculated seawater or a combination of both (Moore 2010). Fresh groundwater delivers new water along with dissolved constituents, while recirculated saline groundwater can deliver large amounts of recycled carbon and nutrients to surface waters (Weinstein et al. 2007; Gleeson et al. 2013; Liu et al. 2014). The fresh and recirculated marine components of SGD are often well mixed, thus making quantification of their relative contribution to coastal waters complex.

Previous studies exploring SGD inputs of dissolved carbon have reported that groundwater discharge from aquifers to the estuarine and coastal zones, may be a significant source of CO₂ and CH₄ to the atmosphere (Cai 2011; Atkins et al. 2013; Call et al. 2015). Additionally, pCO₂ and CH₄ in groundwater can be orders of magnitude higher than atmospheric values (Gagan et al. 2002; Cai 2003; Call et al. 2015). However, estuarine carbon budgets have rarely assessed the importance of groundwater discharge as a driver of CO₂, dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). The results from these limited studies clearly demonstrate that groundwater inputs of dissolved carbon
can be significant and warrant quantification in coastal carbon budgets (Porubsky et al. 2014; Wang et al. 2015).

Most previous studies related to groundwater-derived carbon cycling, have been conducted in the USA and Australia, however, there is still a lack of data from a variety of ecosystems, including estuaries in the southern hemisphere (Cai 2003; Liu et al. 2012; Maher et al. 2013a). Prior studies have attempted to estimate groundwater-derived fluxes of DIC (Atkins et al. 2013), DOC (Goñi and Gardner 2003; Kim et al. 2011), alkalinity (Steward et al., 2015; Cyronak et al. 2014), DIC and DOC (Santos et al. 2012a; Maher et al. 2013a; Porubsky et al. 2014) or DIC and alkalinity (Santos et al., 2015; Liu et al. 2014; Wang et al. 2015) into coastal waters. To our knowledge, no previous study has attempted to simultaneously quantify groundwater-derived inputs of the four main dissolved carbon species (DIC, DOC, CO₂ and CH₄) and alkalinity into an estuary, and the relative importance of groundwater carbon inputs to atmospheric evasion of CO₂ and CH₄ and carbon exports to the coastal ocean.

We hypothesize that groundwater discharge into a small subtropical estuary will be a significant pathway for carbon exported to the coastal ocean. We tested this hypothesis by performing time series measurements of carbon parameters (DIC, DOC, pCO₂, pCH₄), alkalinity, ²²²Rn and Ra isotopes in a tidal estuary that has a simple geometry. Our objectives were to (1) estimate atmospheric CO₂ and CH₄ evasion rates from the estuary, (2) calculate groundwater-derived inputs to the estuary of the four main dissolved carbon species and alkalinity under contrasting hydrological conditions (wet season and dry season), (3) quantify the relative importance of meteoric fresh, and recirculated saline groundwater-derived carbon inputs to the estuary, and (4) determine the relative importance of groundwater in the total carbon and alkalinity exports from the estuary to the coastal ocean. This study builds on a companion paper reporting a detailed radon and radium isotope investigation in the same system (Sadat-Noori et al., 2015).

3.2 Materials and method

3.2.1 Site description

The investigation was carried out in Korogoro Creek (latitude -31.04781°, longitude 153.06492°), a small (5 km long, ~ 20-25 m wide, average depth 0.9 m, area 116,160 m²) subtropical tidal estuary in Hat Head, NSW, Australia (Figure 3.1). The estuary has a small
catchment (18 km²) which is low lying and subject to flooding by seawater during spring tides. The estuary has a residence time of one day and is normally flushed during each tidal cycle, with ocean water penetrating the lower 4 km of the estuary at high tide (Ruprecht and Timms 2010). The region has an average annual rainfall of 1,490 mm and experiences a mild subtropical climate all year round. January and July have the highest (26.9°C) and lowest (11.2°C) monthly mean air temperatures, respectively. Rainfall is highest from February to March (175.2 mm month⁻¹) and lowest from July to September (71 mm month⁻¹) (http://www.bom.gov.au). Our most downstream station was located at the mouth of the estuary (153°3’27.268”E; 31°3’24.801”S) at a sandy beach environment, while the rest of the stations were surrounded by fringing mangrove vegetation.

**Figure 3.1** Study site (Had Head, NSW, Australia) displaying the time series stations (green points) and groundwater sampling locations (red points). The distance between stations 1 - 2 and 2 - 3 is 1.5 km, while stations 3 - 4 are 1 km apart. The dark box represents the study site. The entire estuary length was fringed by mangroves. All carbon species were measured in Station 1, while only $p$CO₂ data are available for Stations 2-4. Image from Google Earth.
3.2.2 Experimental design

Two field campaigns were carried out over two seasons (wet and dry). The first set of time series data collection (wet season) was conducted from 08:45 am March 25th to 10:15 am March 27th 2013, while the second field campaign (dry season) was carried out from 20:30 June 6th to 10:00 am June 10th 2013. Both field campaigns were conducted around the spring tides. However, the tidal range between the semi-diurnal tides varied. During the wet season the tidal range was similar between the semi-diurnal tides (~1.2m), while in the dry season the tidal range varied between ~ 0.6 and 1m (Figure 3.2) over the semi-diurnal tides.
Figure 3.2 Surface water time series data from the downstream station located at the mouth of the estuary in the wet (March) and dry (June) seasons. The radon data are reported in our companion paper Sadat-Noori et al. (2015).
During the first field campaign, we deployed automatic high frequency time series monitoring stations at four approximately equally spaced sites (~1 to 1.5 km apart) along the length of the estuary (Figure 3.1). During the second field campaign, two time series monitoring stations were deployed. The station at the mouth of the estuary, hereafter referred to as “downstream station” continually monitored salinity, temperature, dissolved oxygen, current velocity, \( pCO_2 \), \( pCH_4 \) and \( ^{222}\text{Rn} \), during the two field campaigns, while the other stations measured the same suite of parameters with the exception of \( pCH_4 \). A time series of discrete samples for DIC, DOC and TAlk were also collected from the downstream station every hour over 2 consecutive tidal cycles (> 25 hours) during both sampling campaigns. Groundwater samples were collected throughout the catchment (Figure 3.1) by installing shallow piezometers (Charette and Allen, 2006) and by sampling deep monitoring wells in the region to characterise the groundwater endmember concentration. A mass balance model was developed to evaluate fresh and saline groundwater-derived carbon and alkalinity fluxes, atmospheric exchange rates of \( CO_2 \) and \( CH_4 \), and to quantify carbon exports from the estuary.

### 3.2.3 Surface water time series observations

A calibrated Hydrolab automatic logger was used to measure pH (± 0.02 units), salinity (± 0.02 ppt), dissolved oxygen (± 0.2 mg L\(^{-1}\)), and water temperature (± 0.10 °C), at 15 min intervals, at all stations, during both sampling campaigns. Depth loggers (CTD divers – Schlumberger Water Services) measured estuary depth (± 0.01 m), at 10 minute intervals at each of the four stations. Wind speed data were obtained online (www.wunderground.com) from a weather station at 10 m height located at South West Rocks, about 15 km away from the study site. An acoustic doppler current profiler (ADCP; Sontek Argonaut) was installed in the middle of the estuary at the downstream site to measure current velocity and direction of flow averaged over 10 min intervals. This was combined with time specific cross sectional area (adjusted for tidal height) to obtain 10 min discharge estimates assuming that currents across the channel were homogenous. At the other three time series stations, current velocity was measured using Starflow Ultrasonic Doppler Flow Recorders. The estuary cross section was measured at high tide using a depth gauge at 2 m width intervals.

For determining \( ^{222}\text{Rn} \) concentrations, hereafter referred to as “radon”, a radon-in-air monitor modified for radon-in-water (RAD 7, Durridge Co.) was used (Burnett et al. 2010 and references therein). Radon was measured every 10 minutes for about 40 hours in the wet season and 60 hours in the dry season. At the downstream station during both seasons, a
cavity ring-down spectrometer (Picarro G2201-i) coupled to a showerhead equilibrator was used to measure $p\text{CO}_2$ and $p\text{CH}_4$ at $\sim 1$ Hz (Maher et al. 2013b) with data averaged over 1 minute intervals. The equilibrated air is continuously pumped in a closed-loop from the headspace of the equilibrator chamber through desiccant (Drierite), the cavity ring-down spectrometer, a RAD7 and then back to the equilibrator. For measuring $p\text{CO}_2$ at other stations, a Li-Cor 820 CO$_2$ analyser coupled to a RAD7 radon monitor was used (Santos et al. 2012b). CH$_4$ partial pressure was converted to concentrations based on the solubility coefficient calculated as a function of temperature and salinity (Wiesenburg and Guinasso, 1979) to allow for easy comparison with previous studies that generally use CH$_4$ concentration rather than partial pressure.

Discrete samples were collected using a sample-rinsed 60 ml polyethylene syringe every hour for about 25 hours from the downstream station in both seasons. Samples collected for DIC and DOC concentrations were filtered through 0.7 µm Whatman GF/F filters into acid-rinsed, milli-q rinsed, precombusted (4 hours 400ºC) 40 ml volatile organic carbon borosilicate vials containing 100 µl of saturated HgCl$_2$ without any head space or bubbles. Samples for alkalinity (TAlk) were filtered through 0.7 µm Whatman GF/F and collected in 30 ml polycarbonate vials. The samples were stored on ice until returning to the lab where they were stored at 4 ºC until analysis.

### 3.2.4 Groundwater Sampling

Groundwater sampling was performed at the same time as surface water sampling in both field campaigns. Samples were collected using a push point piezometer system (Charette and Allen 2006). The tubing was thoroughly flushed with the sample prior to collecting each sample. DOC, DIC and TAlk were sampled as per surface water methods described earlier. For radon, shallow wells ranging between 0.5 – 2 m deep were dug adjacent to the estuary near each time series station (Figure 3.1), using a hand held auger at low tide. PVC pipes with 50 cm long slotted screens were installed to allow groundwater infiltrate into the pipe. In addition, deep (5 – 21 m) monitoring wells installed by the NSW Office of Water located across the catchment were also sampled (Figure 3.1). A peristaltic pump was used to take samples after the wells were purged (3 times the casing volume). Groundwater samples are the same as those used for radium isotope and radon concentrations in Sadat-Noori et al. (2015).
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Samples for CO\(_2\) and CH\(_4\) were collected in gas-tight 250 ml bottles, overflowing at least 3 times the bottle volume, to which 200 µL of saturated HgCl\(_2\) solution was added. A calibrated handheld YSI multiprobe was used to determine pH, temperature, DO and salinity for each groundwater sample. A total of 27 groundwater samples were collected. 6 liter gas-tight HDPE plastic bottles were used to collect samples for groundwater radon analysis. Each 6 liter bottle was connected to a RAD7 radon monitor and given at least 2 hours to achieve an air-water radon equilibrium with <5% uncertainty following well established protocols (Lee and Kim 2006). After radon analysis, the water was filtered through magnesium impregnated acrylic fibers for radium analysis (Peterson et al. 2009). Groundwater samples were classified in two classes; deep (>5 m) and shallow (<5 m) based on the radium data in the companion paper (Sadat-Noori et al., 2015).

### 3.2.5 Analytical Methods

Groundwater CO\(_2\) and CH\(_4\) samples were analysed via a headspace method using a Picarro G2201-i as described by Gatland et al. (2014). Analysis for DIC and DOC concentrations were carried out following the wet oxidation method (St-Jean 2003) with an OI Aurora 1030W interfaced with a Therma Delta V+ Isotope Ratio Mass Spectrometer (IRMS) (Maher and Eyre 2011). TA\(_{\text{alk}}\), (± 0.2%) was measured by Gran Titration using a Metrohm automatic titrator and 0.01M HCl standardized to Dickson Certified Reference Material (Batch 111). Free CO\(_2\) within the estuary was determined by using the DIC and TA\(_{\text{alk}}\) pair, and also the pCO\(_2\) and TA\(_{\text{alk}}\) pair, using version 25 of the CO\(_2\)SYS program (Pelletier et al., 2007) with the carbonic acid dissociation constants from Millero et al. (2006) and the KH\(_2\)SO\(_4\) constant from Dickson (1990). Radium samples were collected at the downstream time series station every hour for 30 hours in wet and dry seasons and a Radium Delayed Coincidence Counter (RaDeCC) was used for measuring \(^{223}\)Ra and \(^{224}\)Ra based on Moore and Arnold (1996). Radium data and estimated groundwater discharge rates are presented in a companion paper (Sadat-Noori et al., 2015).

### 3.2.6 Calculations

The CO\(_2\) and CH\(_4\) atmospheric exchange were estimated following Wanninkhof (1992):

\[
\text{Flux} = k\alpha (C_{\text{water}} - C_{\text{air}})
\] (1)
where $C_{\text{water}}$ and $C_{\text{air}}$ are the partial pressure of CO$_2$ or CH$_4$ in the water column and in air, respectively, in units of µatm; $\alpha$ is the solubility coefficient, calculated as a function of temperature and salinity using the constants of Weiss (1974) for CO$_2$ and Wiesenburg and Guinasso, (1979) for CH$_4$. $k$ is the gas transfer velocity at the water–air boundary (m d$^{-1}$). The atmospheric $p$CO$_2$ and $p$CH$_4$ were assumed to be constant at an average of 400 and 1.8 µatm, respectively. We used an empirical equation which estimates transfer velocity as a function of water depth, current and wind speed, which are the dominant sources of water turbulence in estuarine systems (Borges et al., 2004):

$$k_{600} = 1 + 1.719W^{0.5}D^{-0.5} + 2.58U_{10}$$

(2)

where $k_{600}$ is the transfer velocity (normalised to a Schmidt number of 600), $W$ is the water current (cm s$^{-1}$); $D$ is water depth (m) and $U_{10}$ is the wind speed at a height of 10 m (m s$^{-1}$). The Schmidt number is defined as the ratio between the kinematic viscosity to mass diffusivity. All $k_{600}$ values were corrected for the Schmidt number of CO$_2$ and CH$_4$ at in situ temperatures and salinities (Wanninkhof 1992), assuming a linear relationship between salinities of 0 and 35. The main uncertainty associated with quantifying air-water gas exchange results from the estimation of gas transfer velocity ($k$). Most previous studies have used empirical equations which calculate transfer velocity only as a function of wind speed. The model used in this study incorporates current and wind induced turbulence at the air-water interface.

The hourly estuarine export (ebb tide) and import (flood tide) of the four dissolved carbon species (DIC, DOC, free CO$_2$ and CH$_4$) and total alkalinity was estimated by multiplying hourly discharge rates by the carbon species concentration. Daily averages where calculated by integrating export and import rates over 2 tidal cycles then dividing by total time for the 2 tidal cycles (~ 25 hours) to get an hourly rate, and multiplying by 24 (hours in one day) to obtain a daily rate. Groundwater carbon fluxes were calculated by multiplying the corresponding daily volumetric groundwater discharge in each season obtained from Sadat-Noori et al. (2015) by the median concentration of different carbon species in groundwater following Equation (3):

$$GW_{\text{C flux}} = GW_{\text{dis}} \times GW_{\text{med. C conc.}}$$

(3)
where GW$_C$ flux is groundwater carbon fluxes, GW$_{dis}$ is groundwater discharge in each season and GW$_{med.}$ C conc. is median concentration of different carbon species in groundwater. The median concentration was used due to the non-normal distribution of the groundwater endmember concentrations.

A non-steady state radium mass balance was applied to quantify fresh and saline discharging groundwater into the estuary. The model details and results are presented in a companion paper (Sadat-Noori et al., 2105). Briefly concentrations of radium in surface water are converted into net fluxes of groundwater, discharging into the estuary over a 24h diel cycle. Inputs to the model were groundwater, upstream $^{223}$Ra input flux during flood tide, diffusion from sediments and desorption from suspended sediments while outputs consisted of $^{223}$Ra downstream output flux during ebb tides and the $^{223}$Ra decay.

### 3.3 Results

#### 3.3.1 Hydrological conditions

Contrasting hydrological conditions occurred during each field campaign. Two months prior to the time series measurements in the March (wet season) the area received 612 mm of rainfall. The June 2013 (dry season) time series deployment had base flow conditions with only 57 mm of rain in the two months prior to field campaign. As a result, the groundwater level during March was 100 cm higher than in June. Based on the rainfall events of the area and for simplicity, we describe the first and second field campaigns as wet and dry seasons respectively. Surface freshwater discharge (i.e. net freshwater discharge out of the mouth of the estuary) was $3 \text{ m}^3 \text{s}^{-1}$ in the wet season and decreased to $2.2 \text{ m}^3 \text{s}^{-1}$ in the dry season. Wet season had an average surface water temperature of $25.9 \degree C$ compared to $19.4 \degree C$ in the dry season. Wind speeds were on average 3.1 and 1.7 m s$^{-1}$ during the wet and dry seasons, respectively (Figure 3.2). Tidal range was ~ 1.2 m in the wet season while in the dry season the tidal range varied between 1 m and 0.6 m (Figure 3.2). Salinity showed a tidal trend and ranged from nearly fresh (1) to saline (up to 35) over a tidal cycle (Figure 3.2). Salinity increased rapidly during the start of the flood tide just taking 2.5 hours to reach 34 and dropped more slowly during ebb tide taking about 5 hours to reach minimum values. Similar salinity trends were observed in both campaigns.
3.3.2 Groundwater observations and discharge rates

Shallow and deep groundwater dissolved carbon concentrations were highly variable (Table 3.1). Median DIC, DOC and TA\text{lk} in shallow groundwater were 1.1, 1.2 and 1.5 times higher than deep groundwater. Median $p$\text{CO}_2 in deep samples (21,109 µatm) was similar to median $p$\text{CO}_2 in shallow samples (20,924 µatm), while median CH\text{4} concentration was 6.6 times higher in the deep samples (53 µM) than shallow (8 µM).
### Table 3.1 Groundwater observations.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Date</th>
<th>Longitude</th>
<th>Latitude</th>
<th>Depth (m)</th>
<th>Salinity</th>
<th>pH</th>
<th>$^{222}\text{Rn}$ (Bq m$^{-3}$)</th>
<th>Alkalinity (µM)</th>
<th>DIC (µM)</th>
<th>DOC (µM)</th>
<th>Free CO$_2$ (µM)</th>
<th>CH$_4$ (µM)</th>
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<tr>
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<td>30.9</td>
<td>8.5</td>
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<td>2707</td>
<td>2055</td>
<td>271</td>
<td>3</td>
<td>0.02</td>
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<td>E153.056</td>
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<td>8.5</td>
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<tr>
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<td>S31.057</td>
<td>E153.056</td>
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<td>8.2</td>
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</tr>
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<td>12/06/2013</td>
<td>S31.0002</td>
<td>E153.0324</td>
<td>4</td>
<td>0.1</td>
<td>5.0</td>
<td>365</td>
<td>188</td>
<td>3345</td>
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<tr>
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<td>E153.032</td>
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**Total**

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</table>
The discharging groundwater into the estuary surface water was separated into shallow saline and deep fresh groundwater components. Depth was used as a separation factor rather than salinity because in a tidal estuary with a short resident time salinity may not truly represent the spatial groundwater distribution along the estuary. For example, tidal pumping at the downstream station would cause high salinities in shallow groundwater, while the salinity in groundwater samples at station 4 were never higher than 5. Moreover, the 5 m indicator used as a separation was based on the fact that radium concentration was generally higher in samples collected below 5 m (see Sadat-Noori et al. 2015).

Separate discharge rates were estimated based on $^{223}$Ra and $^{224}$Ra for wet and dry seasons and deep and shallow groundwater discharge. An average of the $^{223}$Ra and $^{224}$Ra rates was used to calculate seasonal deep and shallow groundwater discharge rates which were then used to calculate groundwater-derived carbon fluxes entering estuary surface water (refer to Sadat-Noori et al., 2015 for groundwater discharge calculations). In the wet season, groundwater-derived DIC from fresh deep groundwater was 1.8 times higher than saline shallow groundwater-derived DIC. DOC and alkalinity derived from fresh deep groundwater was 1.7 and 1.3 fold higher than saline shallow groundwater-derived DOC (Table 3.2). Groundwater-derived free CO$_2$ and CH$_4$ were 2.1 and 14 fold higher from fresh deep groundwater compared to shallow. In the dry season, DIC, DOC, alkalinity and free CO$_2$, from saline shallow GW were 6.2, 6.3, 8.8 and 5.3 times higher than the fresh deep groundwater fluxes while CH$_4$ fluxes were similar from both deep and shallow fluxes. All estimates of groundwater-derived carbon inputs to the estuary were higher in the wet season (Table 3.2).
**Table 3.2** Groundwater-derived carbon species into the estuary in units of mmol m$^{-2}$ of estuary d$^{-1}$. SGD rates reported in Sadat-Noori et al. (2015) were used.

<table>
<thead>
<tr>
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<th>Wet</th>
<th>Dry</th>
</tr>
</thead>
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<td><strong>Shallow saline</strong></td>
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<tr>
<td>SGD (m$^3$ s$^{-1}$)</td>
<td>0.33±0.09</td>
<td>0.19±0.23</td>
</tr>
<tr>
<td>DIC (mmol m$^{-2}$ d$^{-1}$)</td>
<td>376±376</td>
<td>213±129</td>
</tr>
<tr>
<td>DOC (mmol m$^{-2}$ d$^{-1}$)</td>
<td>322±322</td>
<td>183±521</td>
</tr>
<tr>
<td>Alkalinity (mmol m$^{-2}$ d$^{-1}$)</td>
<td>94±94</td>
<td>53±193</td>
</tr>
<tr>
<td>Free CO$_2$ (mmol m$^{-2}$ d$^{-1}$)</td>
<td>244±244</td>
<td>138±177</td>
</tr>
<tr>
<td>CH$_4$ (mmol m$^{-2}$ d$^{-1}$)</td>
<td>2±2</td>
<td>1±9</td>
</tr>
<tr>
<td><strong>Deep fresh</strong></td>
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<td></td>
</tr>
<tr>
<td>SGD (m$^3$ s$^{-1}$)</td>
<td>0.71±0.25</td>
<td>0.03±0.01</td>
</tr>
<tr>
<td>DIC (mmol m$^{-2}$ d$^{-1}$)</td>
<td>702±97</td>
<td>34±97</td>
</tr>
<tr>
<td>DOC (mmol m$^{-2}$ d$^{-1}$)</td>
<td>564±730</td>
<td>29±730</td>
</tr>
<tr>
<td>Alkalinity (mmol m$^{-2}$ d$^{-1}$)</td>
<td>127±71</td>
<td>6±71</td>
</tr>
<tr>
<td>Free CO$_2$ (mmol m$^{-2}$ d$^{-1}$)</td>
<td>527±110</td>
<td>26±110</td>
</tr>
<tr>
<td>CH$_4$ (mmol m$^{-2}$ d$^{-1}$)</td>
<td>28±17</td>
<td>1±17</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SGD (m$^3$ s$^{-1}$)</td>
<td>1.04±0.13</td>
<td>0.22±0.13</td>
</tr>
<tr>
<td>DIC (mmol m$^{-2}$ d$^{-1}$)</td>
<td>1131±83</td>
<td>243±83</td>
</tr>
<tr>
<td>DOC (mmol m$^{-2}$ d$^{-1}$)</td>
<td>889±436</td>
<td>191±587</td>
</tr>
<tr>
<td>Alkalinity (mmol m$^{-2}$ d$^{-1}$)</td>
<td>211±110</td>
<td>45±148</td>
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<tr>
<td>Free CO$_2$ (mmol m$^{-2}$ d$^{-1}$)</td>
<td>777±104</td>
<td>167±139</td>
</tr>
<tr>
<td>CH$_4$ (mmol m$^{-2}$ d$^{-1}$)</td>
<td>20±10</td>
<td>4±14</td>
</tr>
</tbody>
</table>

Estuary area: 116,160 m$^2$; Catchment area: 18,000,000 m$^2$

### 3.3.3. Estuary surface water time series measurements

Dissolved oxygen (DO) followed a clear tidal trend with the highest values at high tide (Figure 3.2). DO reached 100% saturation at high tide in both seasons and dropped to 50 and 30% at low tide during the dry and wet seasons, respectively. Radon, $p$CO$_2$ and CH$_4$ followed a tidal trend in both seasons with the highest concentrations being recorded at low tide and lowest at high tide (Figure 3.2). Radon concentrations ranged from 0.6 to 180.2 Bq m$^{-3}$ with
an average of 50.5 Bq m$^{-3}$ in wet season and varied between 6.2 to 209.1 Bq m$^{-3}$ with an average of 86.5 Bq m$^{-3}$ in dry season, respectively (Figure 3.2).

DOC followed a tidal trend with high concentrations at low tide and low concentrations at high tide (Figure 3.2), while DIC and TAlk concentrations displayed an opposite tidal trend (high concentrations at high tide). DIC concentrations ranged from 809 to 2,151 µM with an average of 1,558 µM in wet conditions and 1,500 µM in the dry season (Figure 3.2). DOC ranged from 38 to 2,158 µM with an average of 931 µM in the wet season and 668 µM in the dry season. Alkalinity varied between 840 and 2,347 µM with a similar average in both seasons.

Carbon dioxide was the only carbon species with observations in multiple stations along the estuary. At the downstream station, $pCO_2$ followed a tidal trend and was 1.5 times higher in the wet season compared to the dry season (Figure 3.3). Average $pCO_2$ at stations 2, 3 and 4 was about 14,000 µatm in the wet season. Average $pCO_2$ for station 2 in the dry was 9,549 µatm. Maximum $pCO_2$ in surface waters was 25,130 µatm in the wet season (station 2) and 16,764 µatm in the dry season (Figure 3.3). CH$_4$ concentrations (station 1 only) ranged from 5 nM (high tide) to about 3 µM (low tide), while in the dry season CH$_4$ varied between 5 nM (high tide) to 4.8 µM (low tide).
Figure 3.3 Time series of partial pressure of CO$_2$ from the four stations in the wet season, and two stations in the dry season.

### 3.3.4. CO$_2$ and CH$_4$ water to air fluxes

Stations 1, 2, 3 and 4 had average gas transfer velocities ($k_{600}$) values of 4.6, 3.0, 4.4 and 3.1 m d$^{-1}$ respectively, in the wet season while stations 1 and 2 had $k_{600}$ values of 1.7 and 2.9 m d$^{-1}$, respectively, in the dry season. In the wet season, CO$_2$ fluxes from the lower, mid and upper estuary were estimated to be 573 (station 1 average), 1505 (average of station 2 and 3) and 1650 mmol m$^{-2}$ d$^{-1}$ (average of station 3 and 4), respectively. In the dry season the average was 220 for station 1 and 1300 mmol m$^{-2}$ d$^{-1}$ for station 2 (no upper estuary values in dry season, due to vandalism). Wet and dry seasons had an integrated average CO$_2$ flux of 1128 and 620 mmol m$^{-2}$ d$^{-1}$ (Table 3.3). CH$_4$ fluxes from the downstream station were 17 and 43 mmol m$^{-2}$ d$^{-1}$ in wet and dry seasons respectively (Table 3.3).
Chapter 3 | Groundwater discharge as a source of dissolved carbon and greenhouse gases in a subtropical estuary

**Table 3.3** Average gas transfer velocity used in calculations (Equation 2), CO$_2$ and CH$_4$ evasion from the estuary (Equation 1) and groundwater-derived CO$_2$ evasion (Equation 3) in areal units of mmol m$^{-2}$ of estuary d$^{-1}$ and estuary wide units of mmol d$^{-1}$.

<table>
<thead>
<tr>
<th>Season</th>
<th>Average gas transfer velocity</th>
<th>CO$_2$ atmospheric fluxes</th>
<th>GW-derived CO$_2$</th>
<th>CH$_4$ atmospheric fluxes</th>
<th>GW-derived CH$_4$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>m d$^{-1}$</td>
<td>mmol d$^{-1}$</td>
<td>mmol m$^{-2}$ d$^{-1}$</td>
<td>mmol d$^{-1}$</td>
<td>mmol m$^{-2}$ d$^{-1}$</td>
</tr>
<tr>
<td>Wet - (March)</td>
<td>3.0</td>
<td>13.1×10$^7$</td>
<td>1127.7</td>
<td>777</td>
<td>0.2×10$^7$</td>
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<tr>
<td>Dry - (June)</td>
<td>2.3</td>
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<td>619.8</td>
<td>167</td>
<td>0.5×10$^7$</td>
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<tr>
<td>Average</td>
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<td>10.1×10$^7$</td>
<td>869.4</td>
<td>472</td>
<td>0.3×10$^7$</td>
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</table>

3.3.5. Estuarine carbon export

The Hat Head estuary exported on average 20 ± 4 and 9 ± 2 mmol C m$^{-2}$ of catchment d$^{-1}$ of DIC and DOC, respectively, to the coastal ocean (Table 3.4) based on the two field campaigns. DIC, DOC, TAlk and free CO$_2$ exports were 35%, 80%, 30% and 93%, higher in the wet season compared to the dry season, while CH$_4$ was 50% higher in the dry season. Average alkalinity export (23 ± 5 mmol m$^{-2}$ of catchment d$^{-1}$), was similar to DIC and ~ 6 times higher than free CO$_2$ (4 ± 1 mmol C m$^{-2}$ of catchment d$^{-1}$) and several orders of magnitude higher than CH$_4$ (0.005 ± 0.001 mmol C m$^{-2}$ of catchment d$^{-1}$).
Table 3.4 Carbon export from the estuary in units of mmol d$^{-1}$ and carbon yield in mmol m$^{-2}$ of catchment d$^{-1}$.

<table>
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<tr>
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<th></th>
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<td>Shallow GW contribution (mmol d$^{-1}$)</td>
<td>Deep GW contribution (mmol d$^{-1}$)</td>
<td>mmol d$^{-1}$</td>
<td>mmol m$^{-2}$ d$^{-1}$</td>
<td>Shallow GW contribution (mmol d$^{-1}$)</td>
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<tr>
<td>DIC</td>
<td>43.5×10$^7$</td>
<td>±8.6×10$^7$ (26) *</td>
<td>43.6×10$^6$±43.6×10$^6$</td>
<td>81.5×10$^6$±11.2×10$^6$</td>
<td>28.2×10$^7$</td>
<td>±5.6×10$^7$ (16) *</td>
<td>15.6×10$^6$±1.1×10$^6$</td>
<td>4.0×10$^6$±1.1×10$^6$</td>
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<tr>
<td></td>
<td>19.8±3.8</td>
<td>77.0×10$^6$±31.9×10$^6$</td>
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<tr>
<td>DOC</td>
<td>25.5×10$^7$</td>
<td>±5.0×10$^7$</td>
<td>14.1±2.7</td>
<td>37.4×10$^6$±37.4×10$^6$</td>
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<td>Alkalinity</td>
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<td>70.5×10$^6$±82.5×10$^6$</td>
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<td>19.0±3.7</td>
</tr>
<tr>
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<td>23.0±4.5</td>
<td>16.3×10$^6$±18.8×10$^6$</td>
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<td></td>
</tr>
<tr>
<td>Free CO$_2$</td>
<td>13.8×10$^7$</td>
<td>±2.6×10$^7$</td>
<td>7.6±1.4</td>
<td>28.4×10$^6$±28.4×10$^6$</td>
<td>61.3×10$^6$±12.8×10$^6$</td>
<td>0.9×10$^7$</td>
<td>±1.8×10$^6$</td>
<td>0.5±0.1</td>
</tr>
<tr>
<td></td>
<td>4.0±0.7</td>
<td>35.1×10$^6$±58.8×10$^6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.009±10$^7$</td>
<td>0.005</td>
<td>2.2×10$^7$±2.2×10$^7$</td>
<td>3.2×10$^6$±2.0×10$^6$</td>
<td>0.02×10$^7$</td>
<td>±0.1</td>
<td>0.1×10$^6$±1.0×10$^6$</td>
<td>0.2×10$^6$±1.0×10$^6$</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>0.5×10$^6$±2.1×10$^6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Values in bracket indicate calculated DIC using TA and pCO$_2$; Estuary area: 116160 m$^2$; Catchment area: 18,000,000 m$^2$; Groundwater contribution to carbon flux was calculated by dividing the groundwater export (Table 3.6) by the estuary export flux. [i.e. groundwater contribution to DIC export: 687 mmol m$^{-2}$ of estuary d$^{-1}$ / (35.8×10$^7$ mmol d$^{-1}$ / 116160 m$^2$)]
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3.4. Discussion

3.4.1. Carbon data integrity
As we over constrained the carbonate system we investigate the reliability of our measured DIC data by comparing measured DIC concentrations with those calculated from $pCO_2$ and TAlk (Figure 3.4). Our comparison showed that calculated DIC concentrations were on average 9% higher than measured DIC concentration in 90% of the surface water samples. However, for fresh groundwater DIC samples, calculated and measured concentrations showed a closer agreement (Figure 3.4b). The lower measured DIC concentrations may be due to CO$_2$ losses through contact to air at the time of sampling and filtration, and/or, due to an overestimation of calculated DIC due to the contribution of organic acids to the TAlk pool (Hunt et al., 2011, Abril et al., 2015). In spite of these uncertainties, the estimated estuary DIC export rates are similar using both calculated and measured DIC, with only a 8% and 6% higher export rate using the calculated DIC values in the wet and dry season respectively (Table 3.4).

Figure 3.4 Calculated versus measured DIC in surface water and groundwater from the downstream station located at the mouth of the estuary in wet and dry seasons. The line represents the 1:1 ratio.

3.4.2. Carbon water to air fluxes
Water to air CO$_2$ and CH$_4$ fluxes over the study period show that Hat Head estuary was a source of CO$_2$ (620 to 1128 mmol m$^{-2}$ d$^{-1}$) and CH$_4$ to the atmosphere (17 to 43 mmol m$^{-2}$ d$^{-1}$)
(Table 3.3). Atkins et al. (2013) reported similarly high CO$_2$ fluxes of 800 mmol m$^{-2}$ d$^{-1}$ in the upper North Creek Estuary, NSW, Australia with a smaller $k$ value of 2.8 m d$^{-1}$. Frankignoulle et al. (1998), found that nine European estuaries had a mean CO$_2$ flux of 170 mmol m$^{-2}$ d$^{-1}$ using a $k$ value of 1.9 m d$^{-1}$. The average CO$_2$ emission from ten Brazilian estuaries was reported to be 55 ± 45 mmol m$^{-2}$ d$^{-1}$ with $p$CO$_2$ varying between 168 to 8,638 µatm (Noriega and Araujo 2014). We calculated fluxes based on empirical models of $k$ similar to Atkins et al. (2013) and Noriega and Araujo (2014), while Frankignoulle et al. (1998) used the floating chamber method. The global average $p$CO$_2$ in upper estuaries is estimated to be 3033 ± 1078 µatm with a corresponding atmospheric CO$_2$ flux of 188 ± 70 mmol m$^{-2}$ d$^{-1}$ (Chen et al., 2012). In our case, the CO$_2$ water to air flux from the upper estuary (1650 mmol m$^{-2}$ d$^{-1}$) was an order of magnitude higher than the estimated global average. The high fluxes in this study are likely to be directly related to groundwater inputs (see below).

Several previous studies have utilized a fixed time series measuring station usually located at the mouth of the estuary to estimate CO$_2$ and/or CH$_4$ flux for the entire area of the estuary (Bouillon et al. 2007; Maher et al. 2013a). While time series measurements have the advantage of capturing temporal variation with very high resolution, they may not be representative of estuary-wide fluxes due to the inability to account for spatial variation. Maher et al. (2015) suggested that multiple time series stations or a combination of both time series and survey methods may be required to adequately constrain the variability of estuarine CO$_2$ and CH$_4$ fluxes at the estuary scale. Here, we simultaneously deployed four fixed time series stations approximately 1.5 km apart along the length of the estuary (~ 5 km) to cover both temporal and spatial variability, thus providing a more robust estimate of the estuary-wide CO$_2$ dynamics. A similar sampling strategy could not be applied to CH$_4$ and other carbon species due to logistic reasons.

Our multi-station approach demonstrated the importance of spatial variability in estuarine $p$CO$_2$, when calculating estuary-wide fluxes. We estimated CO$_2$ fluxes using four automated measuring stations in the wet season and two stations in the dry season. If we would have only used a single station at the mouth of the estuary, CO$_2$ fluxes upscaled to the entire estuary would be underestimated by 50% and 65% during the wet and dry seasons respectively, (573 and 220 mmol m$^{-2}$ d$^{-1}$, for wet and dry seasons), however, still an order of magnitude higher than the global average estimate for lower estuaries (19 – 59 mmol m$^{-2}$ d$^{-1}$) (Borges and Abril 2011; Cai 2011; Chen et al. 2013). This was calculated following equation (1) by assuming that the downstream station represented a partial pressure of CO$_2$ and $k$ value
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for the entire estuary (i.e. the downstream flux was applied to the entire estuary area). By using the 4 stations, the estuary could be fragmented, with each section having a site-specific set of partial pressures and piston velocities. On the other hand, if sampling had been conducted only in the upstream section of the estuary, CO₂ fluxes would be overestimated considerably. This clearly demonstrates the importance of collecting spatial data from the lower, middle and upper parts of estuarine systems to be able to estimate a more realistic water-air flux of CO₂ as suggested by previous studies (Wang and Cai 2004; Cai 2011; Maher et al. 2015).

Average CH₄ fluxes from Hat Head estuary were high, averaging 26 mmol m⁻² d⁻¹ (Table 3.3). These fluxes are about 43 times higher, than the higher end of average global methane flux estimates, from tidal estuaries, which range between 0.04 – 0.6 mmol m⁻² d⁻¹ (Borges and Abril 2011). Ferrón et al. (2007) and Zhang et al. (2008) reported an annual average CH₄ flux of 0.66 and 0.61 mmol m⁻² d⁻¹ from tidal estuaries in Bay of Cádiz, SW Spain and Changjiang, China, while Nirmal Rajkumar et al. (2008) reported CH₄ fluxes of 3.6 mmol m⁻² d⁻¹ from an estuarine system (Adyar) in India. Maher et al. (2015) found CH₄ fluxes in a subtropical Australian estuary to be 0.57 mmol m⁻² d⁻¹, Linto et al. (2014) and Call et al. (2015) reported CH₄ fluxes from tidal mangrove estuaries to be 0.35 and 0.21 mmol m⁻² d⁻¹, respectively.

Average CO₂ atmospheric fluxes were 1.8 times higher in wet (1128 mmol m⁻² d⁻¹) than the dry seasons (620 mmol m⁻² d⁻¹) (Table 3.3). This difference may be related to higher temperatures in the wet season (summer) and subsequent higher rates of in situ respiration, and/or nitrification which has a net effect of decreasing alkalinity and pH and therefore increasing pCO₂ (Frankignoulle et al., 1996; Gazeau et al. 2005; Borges and Abril, 2011, Maher and Eyre 2012). Interestingly, water to air CH₄ fluxes where higher in the dry (43 mmol m⁻² d⁻¹) than the wet season (17 mmol m⁻² d⁻¹), driven by higher concentrations (Figure 3.2) rather than higher transfer velocities (Table 3.3). This is in spite of higher groundwater inputs in the wet season (Table 3.2). This may be due to seasonal differences in methane oxidation rate (Abril and Iversen 2002) or alternative sources or production rates of CH₄ within the estuary during the two seasons. Further studies would be required to assess the factors controlling seasonal variability in surface water CH₄ dynamics.

While CO₂ emissions may dominate carbon gaseous fluxes, CH₄ emissions could have a greater impact on global warming potential of the system (Gatland et al. 2014). Although CH₄ losses to the atmosphere were smaller than CO₂, CH₄ is a more potent greenhouse gas
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compared to CO$_2$, therefore, accounting only for CO$_2$ evasion in systems where there may be high CH$_4$ emissions, could result in an underestimation, in terms of global warming potential of the system (Gatland et al. 2014; Panneer Selvam et al. 2014; Neubauer et al., 2015). Here, after CH$_4$ fluxes were converted into CO$_2$-equivalent emission estimates assuming a 100 year CH$_4$ sustained-flux global warming potential [i.e., 1 kg CH$_4$=45 kg of CO$_2$; Neubauer et., al (2015)], CH$_4$ accounted for ~ 50% of CO$_2$-equivalent emissions from the estuary for both seasons, and therefore was significant in terms of greenhouse gas emissions.

3.4.3. Carbon surface water exports

Table 3.5 presents estimates of DIC and DOC export to coastal waters from small estuarine and large riverine systems. In a review paper, Cai (2011) reported the global riverine DOC export rate to be 246 Tg y$^{-1}$. Bauer and Bianchi (2011) also reported a similar global oceanic DOC export rate (250 Tg yr$^{-1}$). Based on the world wide surface areas of estuaries which is 1.05×10$^{12}$ m$^2$ (Cai 2011), global DOC export from estuarine systems is estimated to be 0.64 g C m$^{-2}$ d$^{-1}$. Hat Head estuary exported 15.5 g C m$^{-2}$ of estuary d$^{-1}$ of DOC, which is 24 times higher than the global estuarine DOC export estimate. DOC export from Hat Head estuary was also higher than much larger riverine systems (Striegl et al. 2007; Cai et al. 2008). Based on Table 3.5, DOC exports from systems of a similar small size to Hat Head estuary are higher, however, it should be noted that exports reported in Adame and Lovelock (2011), Bergamaschi et al. (2012), Maher et al. (2013a), Wang and Cai (2004) and Winter et al. (1996) are from mangrove or salt marsh systems which essentially have a minimal catchment area to water area ratio, thereby inflating the mmol C m$^{-2}$ catchment d$^{-1}$ (i.e. essentially all the catchment is intertidal). Moreover, DIC exports from the small Hat Head estuary had much higher DIC exports than larger riverine systems on a catchment area basis (Table 3.5). Hat Head estuary DIC yield (i.e. export per unit of catchment area), were 4 times higher than the Gulf of Trieste catchment (Tamše et al. 2014), 11–40 times higher than the Yukon River (Striegl et al. 2007), 16 – 55 times higher than the 6 largest Arctic Rivers (Tank et al. 2012) and two orders of magnitude higher than DIC exports reported for the Chena River in Alaska (Cai et al. 2008) and the Guadalquivir Estuary, Spain (De La Paz et al. 2007). In comparison with smaller estuaries, Hat Head DIC yield was two orders of magnitude higher than the York River estuary (Raymond et al. 2000) and comparable with intertidal mangrove and saltmarsh systems (Wang and Cai 2004, Bouillon et al. 2008; Maher et al. 2013a; Winter et al. 1996).
Table 3.5 Previous studies estimating groundwater derived DIC, DOC, TAlk and CH$_4$ using natural tracers. Units are in mmol m$^{-2}$ of estuary d$^{-1}$. Table updated from Atkins et al. (2013).

<table>
<thead>
<tr>
<th>Location</th>
<th>System description</th>
<th>GW-Derived DIC fluxes</th>
<th>GW-Derived DOC fluxes</th>
<th>GW-Derived TAlk fluxes</th>
<th>GW-Derived CH$_4$ fluxes</th>
<th>GW trancing method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hat Head, Australia</td>
<td>Tidal estuary</td>
<td>687.3</td>
<td>540.2</td>
<td>128.1</td>
<td>12.5</td>
<td>Ra isotopes</td>
<td>This study (2015)</td>
</tr>
<tr>
<td>Jiulong River estuary, China</td>
<td>River estuary</td>
<td>121-897</td>
<td></td>
<td>91-748</td>
<td></td>
<td>Ra isotopes</td>
<td>Wang et al. (2015)</td>
</tr>
<tr>
<td>Moreton Bay, Australia</td>
<td>Embayment</td>
<td>153</td>
<td>36</td>
<td>161</td>
<td></td>
<td>Ra isotopes</td>
<td>Stewart et al. (2015)</td>
</tr>
<tr>
<td>Wadden Sea, Germany</td>
<td>Tidal flats</td>
<td>42</td>
<td>1344</td>
<td></td>
<td></td>
<td>$^{222}$Rn</td>
<td>Santos et al. (2015)</td>
</tr>
<tr>
<td>Heron Island, Australia</td>
<td>Coral reef</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td>$^{222}$Rn</td>
<td>O’Reilly et al. (2015)</td>
</tr>
<tr>
<td>Okatee Estuary, USA</td>
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<td>1079</td>
<td>64</td>
<td></td>
<td>0.8</td>
<td>Ra isotopes</td>
<td>Porubsky et al (2014)</td>
</tr>
<tr>
<td>North Creek, Australia</td>
<td>Fresh water tidal creek</td>
<td>1810</td>
<td></td>
<td></td>
<td></td>
<td>$^{222}$Rn</td>
<td>Atkins et al. (2013)</td>
</tr>
<tr>
<td>Moreton Bay, Australia</td>
<td>Mangrove tidal creek</td>
<td>250</td>
<td>24</td>
<td></td>
<td></td>
<td>$^{222}$Rn &amp; $\delta^{13}$C</td>
<td>Maher et al. (2013)</td>
</tr>
<tr>
<td>Heron Island, Australia</td>
<td>Permeable carbonate sediments</td>
<td>1.6-18.8</td>
<td>5.1-8.8</td>
<td></td>
<td></td>
<td>$^{222}$Rn</td>
<td>Cyronak et al. (2013)</td>
</tr>
<tr>
<td>Yarra River, Australia</td>
<td>Salt wedge estuary</td>
<td>349</td>
<td>21</td>
<td></td>
<td></td>
<td>$^{222}$Rn</td>
<td>Santos et al. (2012a)</td>
</tr>
<tr>
<td>Indian River Lagoon, USA</td>
<td>Coastal lagoon</td>
<td>120 - 340</td>
<td></td>
<td></td>
<td></td>
<td>$\delta^{13}$C and $\delta^{14}$C</td>
<td>Dorsett et al. (2011)</td>
</tr>
<tr>
<td>West coast of Florida, USA</td>
<td>Sandy beach</td>
<td>19 - 27</td>
<td></td>
<td></td>
<td></td>
<td>Ra isotopes</td>
<td>Santos et al. (2009)</td>
</tr>
<tr>
<td>Okatee Estuary, USA</td>
<td>Salt marsh/estuary</td>
<td>1963</td>
<td>170</td>
<td></td>
<td></td>
<td>Ra isotopes</td>
<td>Moore et al. (2006)</td>
</tr>
<tr>
<td>North Inlet, USA</td>
<td>Salt marsh/estuary</td>
<td>171</td>
<td></td>
<td></td>
<td></td>
<td>Ra isotopes</td>
<td>Cai et al. (2003)</td>
</tr>
<tr>
<td>South Carolina, USA</td>
<td>Tidal creek</td>
<td>50</td>
<td></td>
<td></td>
<td></td>
<td>Piezometer</td>
<td>Goni and Gardner (2003)</td>
</tr>
</tbody>
</table>
The source of DIC is possibly from the surrounding mangroves, as Hat Heat estuary has an extensive mangrove environment throughout the estuary (Figure 3.1). Mangrove environments tend to have high DIC export rates (Bouillon et al. 2008; Miyajima et al. 2009; Maher et al. 2013a). Moreover, a DIC vs. salinity scatter graph (Figure 3.5) showed a slight concave upward trend (at least in the dry season) which suggests mid-estuary inputs of DIC (perhaps from mangrove groundwater). DOC, however, had a conservative or sink nature in relation to salinity (Figure 3.5), which suggests an upstream source (likely the freshwater wetlands or groundwater, see also Sanders et al., 2015) with some loss during estuarine transport (respiration, photomineralization or flocculation). Our mass balance approach suggests significant groundwater inputs of all dissolved carbon species, yet the traditional salinity mixing model approach does not indicate a clear source. Wang et al. (2015) found a significant groundwater source of DIC in the Jiulong estuary (China), yet salinity versus DIC indicated conservative mixing. The authors suggested that the diffuse nature of SGD-derived solute inputs may lead to no deviation from conservative mixing, which may also be the case in Hat Head estuary, and other estuarine systems that have large areas of diffuse groundwater input along the estuary.
Figure 3.5 DIC, DOC, Alkalinity, $p$CO$_2$ and CH$_4$ vs. radon, salinity and depth in estuary surface water in wet (March) and dry (June) seasons from the downstream station located at the mouth of the estuary. Lines indicate the theoretical conservative mixing.

Alkalinity export to the coastal ocean ranged from 19 to 27 mmol m$^{-2}$ of catchment d$^{-1}$ in dry and wet seasons, respectively (Table 3.4). Previous studies have reported alkalinity exports, from larger systems, however, studies with time series sampling for calculating alkalinity exports from tidal estuaries are still scarce. Faber et al. (2014) identified that DIC export was mostly alkalinity in a mangrove and seagrass dominated tidal creek in southeast
Australia. They reported export rates ranging from 140–460 mmol m$^{-2}$ of water area d$^{-1}$, which was an order of magnitude lower than alkalinity export estimates from Hat Head estuary (3564 mmol m$^{-2}$ of water area d$^{-1}$). Santos et al. (2015) reported groundwater-derived alkalinity exports 4.7 times higher than Hat Head from tidal flats in the Wadden Sea (Germany) where porewater alkalinity concentrations are extremely high at 20 mM. Alkalinity production has a significant influence on the global carbon budgets by affecting the oceanic carbonate system. In the case of alkalinity production, carbon is not lost to the atmosphere as CO$_2$, and is exported to the ocean and acts as a buffer which facilitates the uptake of extra CO$_2$ (Faber et al. 2014).

Table 3.5 shows that a general negative correlation may exist between dissolved carbon yield and catchment area, and that small estuarine systems have the ability to deliver more dissolved organic carbon to the coastal ocean compared to larger riverine systems on a catchment area basis. This is mainly due to the shorter residence time of estuaries which reduces the potential for biogeochemical processes to modify the quantity and composition of organic matter. This highlights the importance of studying small systems with a short residence time, such as Hat Head, to obtain a better quantitative understating of global carbon exports to the ocean.

### 3.4.4. Groundwater-derived carbon fluxes

We could not collect deep groundwater samples during the wet season, and shallow samples were only collected from the most downstream station during the wet season field campaign. We acknowledge the limitations with this approach. However, shallow samples collected at the downstream station were similar during both seasons (averages within 10%), and previous studies have found that deep groundwater has relatively stable composition (Dhar et al., 2008; Chapagain et al., 2010). Further, shallow groundwater only dominates inputs during the dry season (Sadat-Noori et al., 2015), when we have adequate sampling coverage throughout the estuary to constrain the shallow groundwater endmember. Considering the uncertainty in shallow groundwater composition during the wet season (i.e. we have used the dry season data to estimate this), we have assigned a 100% uncertainty to this term in our calculations (Table 3.4). The relative contributions of deep and shallow groundwater carbon inputs during wet and dry seasons basically follows the groundwater discharge rates with deep groundwater dominating carbon inputs in the wet season and shallow groundwater delivering more carbon in the dry season. Groundwater fluxes of each
carbon species could not be calculated for each individual section during each season due to the lack of groundwater and surface water samples in the upper reaches of the estuary. Surface water samples were only collected at the downstream station for carbon parameters other than $p$CO$_2$.

Another limitation to our groundwater fluxes is that the average flux presented here only considers the differences between the wet and dry season while other factors such as differences in spring-neap tide cycles and annual temperature variability may influence the groundwater discharge flux (de Sieyes et al., 2008; Constantz et al., 1994) and estuarine carbon fluxes. Moreover, tidal variability can also influence groundwater discharge rates and consequently carbon fluxes, as tidal pumping releases shallow saline groundwater into the estuary (Call et al., 2015, Maher et al 2015, Santos et al., 2009). Tidal pumping was the dominant source of groundwater discharge in the dry season making the shallow saline groundwater contribution much higher than deep fresh groundwater. Therefore, some of the differences that were observed may be due to differences in tidal pumping.

Most of the carbon input to surface waters via groundwater was in the form of DOC and DIC and the smallest portion was contributed by CH$_4$ (1%) in both seasons (Figure 3.6). The total groundwater-derived DIC flux entering surface waters was 4.6 times higher in the wet season compared to dry. While the total (deep + shallow) average groundwater-derived DIC fluxes from both seasons (687 ± 117 mmol m$^{-2}$ of estuary d$^{-1}$) were comparable to previous studies by Santos et al. (2012a), Dorsett et al. (2011) and Cai (2003) (see Table 3.6), higher DIC fluxes have been reported in salt marshes/estuaries (Moore et al. 2006) and fresh water tidal creeks (Atkins et al. 2013) (Table 3.6). The total (deep + shallow) average (wet and dry) groundwater-derived DOC fluxes found here (540 ± 731 mmol m$^{-2}$ d$^{-1}$) are high, being at least 3 fold higher than previous studies which have reported groundwater-derived DOC fluxes ranging from 21 to 170 mmol m$^{-2}$ d$^{-1}$ (Santos et al. 2012a; Maher et al. 2013a; Porubsky et al. 2014) (Table 3.6). These high fluxes are related to the high DOC concentrations in groundwater (Table 3.1).
**Figure 3.6** Average (wet and dry season) portions of carbon species derived by groundwater and losses from the mouth of the estuary assuming that alkalinity fluxes are related to carbonate alkalinity.
### Table 3.6

Previous studies estimating DIC and DOC export (yield) to coastal waters from small and large estuaries. Units are mmol C m\(^{-2}\) of catchment d\(^{-1}\).

<table>
<thead>
<tr>
<th>Location</th>
<th>Description</th>
<th>Country</th>
<th>Catchment size (km(^2))</th>
<th>DIC export</th>
<th>DOC export</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hat Head</td>
<td>Tidal estuary</td>
<td>AUS</td>
<td>18</td>
<td>19.8</td>
<td>8.5</td>
<td>This study (2015)</td>
</tr>
<tr>
<td>Duplin River, on Sapelo Island</td>
<td>Marsh-dominated estuary</td>
<td>USA</td>
<td>2</td>
<td>24.9*</td>
<td></td>
<td>Wang and Cai (2004)</td>
</tr>
<tr>
<td>Southwest Florida coast</td>
<td>Mangrove-dominated estuary</td>
<td>USA</td>
<td>230</td>
<td></td>
<td>41.1</td>
<td>Bergamaschi et al. (2012)</td>
</tr>
<tr>
<td>Southern Moreton Bay</td>
<td>Mangrove-dominated estuary</td>
<td>AUS</td>
<td>0.4</td>
<td>250.0</td>
<td>25.0</td>
<td>Maher et al. (2013a)</td>
</tr>
<tr>
<td>Average from different mangrove systems</td>
<td>Micro-tidal mangrove</td>
<td>USA</td>
<td></td>
<td></td>
<td>16.7</td>
<td>Adame and Lovelock (2011)</td>
</tr>
<tr>
<td>York River estuary - Chesapeake Bay</td>
<td>River estuary</td>
<td>USA</td>
<td>4</td>
<td>0.67</td>
<td></td>
<td>Raymond et. al. (2000)</td>
</tr>
<tr>
<td>Swartkops estuary</td>
<td>Salt marsh estuary</td>
<td>South Africa</td>
<td>4</td>
<td>247.3</td>
<td>23.5</td>
<td>Winter et al. (1996)</td>
</tr>
<tr>
<td>Jiulong River estuary</td>
<td>River estuary</td>
<td>China</td>
<td>71</td>
<td>2.4 - 3.9</td>
<td></td>
<td>Wang et al. (2015)</td>
</tr>
<tr>
<td>Range of different mangrove systems</td>
<td>Mangrove estuaries</td>
<td></td>
<td>1,992</td>
<td>254.0</td>
<td>34.2</td>
<td>Bouillon et al. (2008)</td>
</tr>
<tr>
<td>Chena River, Alaska</td>
<td>River</td>
<td>USA</td>
<td>5,200</td>
<td>0.9</td>
<td>0.3</td>
<td>Cai et al. (2008)</td>
</tr>
<tr>
<td>Guadalquivir Estuary (SW Iberian Peninsula)</td>
<td>River estuary</td>
<td>Spain</td>
<td>58,000</td>
<td>0.2</td>
<td></td>
<td>de la Paz et al. (2007)</td>
</tr>
<tr>
<td>Gulf of Trieste (North Adriatic)</td>
<td>River</td>
<td>Italy</td>
<td>500</td>
<td>5.0</td>
<td></td>
<td>Tamse et al. (2014)</td>
</tr>
<tr>
<td>Yukon River</td>
<td>River</td>
<td>Canada-USA</td>
<td>853,300</td>
<td>0.5-1.7</td>
<td>0.25-0.4</td>
<td>Striegl et al. (2007)</td>
</tr>
<tr>
<td>6 Arctic rivers</td>
<td>River</td>
<td>Europe</td>
<td>10,900,000</td>
<td>0.35-1.2</td>
<td></td>
<td>Tank et al. (2012)</td>
</tr>
</tbody>
</table>
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$pCO_2$ in the water column was positively correlated with radon (Figure 3.5), indicating that groundwater is a source of free $CO_2$ and/or $[H^+]$. The strong relationship between $pCO_2$, $CH_4$ and radon (groundwater tracer) during both wet and dry season field campaigns (Figure 3.5), in addition to the high groundwater $pCO_2$ and $CH_4$ concentrations, implies groundwater was a major driver of surface water $pCO_2$ and $CH_4$ in Hat Head estuary. This influence could either be directly by discharging $pCO_2$ and $CH_4$ enriched groundwater into the estuary or indirectly by groundwater delivering DOC, which can boost ecosystem respiration and increase $pCO_2$ (Maher et al. 2015). The later process is further supported by the DOC vs. radon plot (Figure 3.5) which shows a positive correlation. The salinity mixing plots (Figure 3.5) show that $pCO_2$ and $CH_4$ have a concave trend with salinity indicating an upstream input likely being groundwater discharge from the upper reaches as this area was found to be a groundwater hotspot in a concurrent study by Sadat-Noori et al., (2015).

Flux calculations offer stronger evidence that groundwater plays a major role in delivering greenhouse gasses to surface waters. The fluxes obtained from the groundwater mass balance approach show that groundwater-derived free $CO_2$ and $CH_4$ inputs can account for a large proportion (54% for $CO_2$ and 46% for $CH_4$) of the observed atmospheric fluxes (Table 3.3). Previous studies have also found groundwater to be a major driver of surface water $pCO_2$ and $CH_4$ (Faber et al. 2014; Macklin et al. 2014; Call et al. 2015). Atkins et al. (2013) reported that groundwater-derived $CO_2$ fluxes into a flood plain creek estuary, NSW, Australia, averaged 1622 mmol m$^{-2}$ d$^{-1}$, a value twice as high as atmospheric $CO_2$ evasion in the area, and 1.5 times larger than $CO_2$ fluxes in our case. Conversely, Porubsky et al. (2014) stated groundwater-derived $CH_4$ fluxes were 0.8 mmol m$^{-2}$ d$^{-1}$ in Okatee estuary in USA, 15 times smaller than fluxes from Hat Head estuary.

Radon also had a positive correlation with DOC especially in the wet season, but not as clear as $pCO_2$ and $CH_4$, likely due to multiple processes driving surface water DOC dynamics in this system. For example, radon and DOC may have the same source (groundwater) but have different loss pathways as radon is a gas and its major loss source is atmospheric evasion, while DOC maybe lost through respiration, flocculation and photomineralization. This creates a decoupling between radon and DOC which may not be so apparent as in the radon vs $CO_2$ and $CH_4$ plots (Figure 3.5) and explains the stronger correlation between radon and the greenhouse gases.

Estuarine $CO_2$ is driven by biological (productivity/respiration), hydrological (groundwater inputs and mixing of riverine and oceanic waters) and physical (temperature
driven groundwater convection and wind driven evasion) process (Borges and Abril 2011; Maher et al. 2015). Here, the contribution of groundwater to CO₂ loss (evasion and export (Table 3.3 and 4)) from the estuary was on average 31% over both seasons. The groundwater contribution to CH₄ loss (evasion and export) was around 46%, with significant differences in wet and dry seasons. This can be explained through the difference in the groundwater discharge rate between wet and dry seasons (Table 3.2), where the groundwater contribution is a function of groundwater discharge (which varied significantly in different hydrological conditions at our site) and groundwater end-member concentration (which was assumed to be the same during both seasons).

Dissolved carbon is transported from groundwater to the estuary and then the atmosphere (CO₂ and CH₄) and the ocean (DIC and DOC). Figure 3.3 illustrates this for CO₂, where oceanic waters enter the estuary with the flood tide, becomes enriched in dissolved carbon within the estuary due to mixing with groundwater (and upstream wetland surface water) and leaves the system via ebb tide flow and atmospheric evasion. By investigating the CO₂ versus salinity plot for the 4 stations (Figure 3.7) we found hysteresis occurring at some stations with different CO₂ values at the same salinity during the ebb and flood tide. For instance, observations at station 3 in the wet season showed that as the salinity starts to decrease from flood tide, CO₂ remains low for 8 hours. This continues until brackish waters occupy the station (salinity ~ 8), implying that the initial fresh water entering the estuary is fresh surface water relatively low in CO₂. A subsequent increase in CO₂ values imply the input of groundwater during the ebb tide, indicating a delayed groundwater input to the estuary. This interpretation is supported by the CO₂ vs. radon scatter that shows no hysteresis (Figure 3.5).


**Figure 3.7** \(\text{CO}_2\) versus salinity scatter plots in wet and dry seasons at the four stations along the estuary showing hysteresis.

Total average groundwater-derived \(\text{CH}_4\) fluxes (12 ± 17 mmol m\(^{-2}\) d\(^{-1}\)) (Table 3.2) were much higher than groundwater-derived \(\text{CH}_4\) fluxes from a small tidal river estuary, in Okatee, USA (0.9 mmol m\(^{-2}\) d\(^{-1}\), Porubsky et al. 2014). They were also three orders of magnitude higher than \(\text{CH}_4\) fluxes on the Florida Gulf Coast (Cable et al. 1996). Groundwater-derived \(\text{CH}_4\) fluxes were accountable for almost all the export from the estuary, and much of the free \(\text{CO}_2\) export could be attributed to groundwater inputs (Table 3.4) indicating the major role of
groundwater in CH₄ and dissolved CO₂ transported between terrestrial and aquatic environments.

Average DIC and DOC export from the estuary (3081 ± 602 and 1317 ± 258 mmol m⁻² d⁻¹, respectively) were 4.4 and 2.4 fold higher than groundwater-derived DIC (687 ± 117 mmol m⁻² d⁻¹) and DOC (540 ± 731 mmol m⁻² d⁻¹) indicating that groundwater can account for almost half of the dissolved organic carbon export from the estuary. In other words, the average contribution of groundwater to DOC export in both seasons was ~ 41% while groundwater contributed ~ 22% to DIC export with considerable differences in wet and dry seasons (Table 3.4). Maher et al. (2013a) also found that groundwater advection was a dominant pathway for DOC export, and was responsible for 90% of DOC export in a mangrove tidal estuary. Faber et al. (2014) reported that 90% of the carbon loss from an estuary system was from groundwater DIC advection while DOC only accounted for 5%. Liu et al. (2014) reported that groundwater DIC fluxes were 11–71 times higher than the combined input of local rivers, suggesting that SGD was the dominant source of DIC to the southwest Florida Shelf, USA. Wang et al. (2015) found that SGD input of DIC to the Jiulong River estuary in China was the equivalent to between 25% and 110% of riverine DIC exports.

Groundwater had a minor contribution to TAlk input into the estuary (~ 3%) in both seasons (Table 3.4). Average alkalinity export from estuary was almost 28 fold higher than groundwater-derived alkalinity inputs, suggesting that processes other than groundwater input are driving alkalinity export from this system. This alkalinity is thought to come from sulphate reduction in shallow porewaters (Faber et al. 2014), however, our groundwater sampling resolution was not adequate to capture this process (alkalinity may be produced in the upper cm of sediments, while our groundwater samples were taken from areas deeper than 1 m).

To summarize the key findings of this study, we present a conceptual diagram (Figure 3.8) that illustrates the (1) groundwater discharge rates, (2) flux estimates of groundwater-derived carbon into the estuary, (3) estuary carbon export and (4) carbon atmospheric evasion in wet and dry conditions in the whole estuary system. The large variability observed in groundwater discharge and carbon loss rates over a relatively short time scale indicates the need for more frequent measurements to be carried to assess the influence of groundwater on carbon cycling. Nevertheless, it is clear that this small wetland-surrounded subtropical estuary has a high carbon yield (in terms of both oceanic export and air-water exchange), and
groundwater carbon inputs play a major role in estuarine carbon cycling in this system. Combined with the recent literature, this investigation demonstrates that groundwater may play a major role in estuarine carbon dynamics.

Figure 3.8 Conceptual diagram of the study area summarizing flux estimates ± standard error of groundwater-derived, estuary export and atmospheric evasion of carbon from the mouth of the estuary in (a) wet and (b) dry seasons. Groundwater discharge rates are in m$^3$ s$^{-1}$ and all other parameters are in units of 10$^4$ mols d$^{-1}$ (estuary area = 116,160 m$^2$ and catchment area = 18 km$^2$).
3.5. Conclusions

The Hat Head estuary, had a high area normalised export rate of DIC (3081 ± 602 mmol m$^{-2}$ d$^{-1}$), DOC (1317 ± 258 mmol m$^{-2}$ d$^{-1}$) and TAlk (3564 ± 705 mmol m$^{-2}$ d$^{-1}$) to the coastal ocean and groundwater-derived carbon inputs were a significant component of this carbon export. Groundwater contribution to carbon loss from the estuary for DIC, DOC, TAlk, free CO$_2$ and CH$_4$ was found to be approximately 22%, 41%, 3%, 75% and 100%, respectively. The average estuary-wide CO$_2$ and CH$_4$ evasion rates were 870 ± 174 and 26 ± 5 mmol m$^{-2}$ d$^{-1}$ (some of the highest estuarine fluxes reported yet), and groundwater discharge accounted for 54% and 46% of these evasions, respectively. Our observations indicate that small estuarine systems with a short residence time can pump more carbon to the coastal ocean compared to some larger riverine systems on a catchment area basis, and that groundwater exchange may deliver large amounts of carbon to surface estuarine waters.
Chapter 4

Fresh Meteoric versus Recirculated Saline Groundwater Nutrient Inputs into a Subtropical Estuary

Abstract

The role of groundwater in transporting nutrients to coastal aquatic systems has recently received considerable attention. However, the relative importance of fresh versus saline groundwater-derived nutrient inputs to estuaries and how these groundwater pathways may alter surface water N:P ratios remains poorly constrained. We performed detailed time series measurements of nutrients in a tidal estuary (Hat Head, NSW, Australia) and used radium to quantify the contribution of fresh and saline groundwater to total surface water estuarine exports under contrasting hydrological conditions (wet and dry season). Average nutrient fluxes showed that the estuary was a source of nutrients to the coastal waters. Dissolved inorganic nitrogen (DIN) export was 7-fold higher than the average global areal flux rate for rivers likely due to the small catchment size, surrounding wetlands and high groundwater inputs. Fresh groundwater discharge was dominant in the wet season accounting for up to 45% of total dissolved nitrogen (TDN) and 48% of total dissolved phosphorus (TDP) estuarine exports. In the dry season, fresh and saline groundwater accounted for 21 and 33% of TDN export, respectively. The combined fresh and saline groundwater fluxes of NO$_3$, PO$_4$, NH$_4$, DON, DOP, TDN and TDP were estimated to account for 66, 58, 55, 31, 21, 53 and 47% of surface water exports, respectively. Groundwater-derived nitrogen inputs to the estuary were responsible for a change in the surface water N:P ratio from typical N-limiting conditions to P-limiting as predicted by previous studies. This shows the importance of both fresh and saline groundwater as a source of nutrients for coastal productivity and nutrient budgets of coastal waters.

**Keywords:** Submarine groundwater discharge, Groundwater–surface water interaction, radium isotopes, nitrogen, phosphorus.
4.1 Introduction

Nutrients are key elements for aquatic life but in excess they can be harmful. High inputs of nutrients into aquatic systems can lead to eutrophication (Urquidi-Gaume et al., 2016) and potentially toxic algal blooms (Sugimoto et al., 2015). Eutrophication leads to an excess of organic matter and increased oxygen demand, which can create anoxic environments. This can cause losses of aquatic species, environmental stress and threatens the ecosystem health (Seitzinger et al., 2005). Eutrophication can occur naturally as a slow aging process for a water body. However, human activity can greatly speed up eutrophication (Delgado-Baquerizo, 2016).

Coastal estuarine ecosystems are among the most productive biological areas in the world (Borges and Abril, 2011; Maher et al., 2012). While surface water runoff through rivers is often considered the main pathway for delivering nutrients to estuaries, submarine groundwater discharge (SGD) is also proven to be a significant source of nutrient transport from the land to coastal and estuarine waters (Burnett et al. 2006; Santos et al., 2014; Su et al., 2014). Previous studies have shown groundwater can be a major source of nutrients to continental margins (Kim and Swarzenski, 2010), coral reef lagoons (Tait et al., 2014), tropical islands (Erler et al., 2014), estuaries (Wong et al., 2013), mangroves (Gleeson et al., 2013) and coastal lagoons (Bernard et al., 2014).

The modern definition of SGD incorporates both fresh terrestrially-driven groundwater and saline recirculated seawater (Moore, 2010), both of which can deliver high nutrient loads to estuaries. Only the terrestrial source of SGD represents new nutrient loads to surface waters. However, the recirculated saline component may contain high concentrations of nutrients because of biological and chemical reaction between saline groundwater and sediments (Moore et al., 2006; Santos et al., 2015). Saline SGD can buffer seasonal inputs of new nutrients and maintain productivity in coastal waters (Billerbeck et al. 2006). The portion of fresh and saline components of SGD can vary significantly based on hydraulic conditions, tidal forcing and distance of the fresh and saline mixing zone from the shore (Taniguchi et al., 2006). These conditions operate on a seasonal time scale and are significantly regulated by wet and dry seasons (Michael et al., 2005). Santos et al. (2009) reported that fresh SGD accounted for only 5% of total water inputs, but 50% of the total dissolved nitrogen inputs via SGD at a beach site in the Gulf of Mexico. Similarly, in a study in the Mediterranean, fresh groundwater was found to be the main conveyor of inorganic nitrogen to the coastal water while the saline component was nutrient-poor (Weinstein et al.,
Kroeger et al. (2008) estimated dissolved inorganic nitrogen from fresh terrestrial SGD was 3.5 times greater than marine source groundwater in Waquoit Bay, Massachusetts, USA. These and similar studies have focused on defining the contribution of different groundwater sources at a regional scale in open systems (i.e., bays or open ocean), but have not focused on estuarine systems.

Groundwater can deliver both dissolved organic nutrients and dissolved inorganic nutrients which react differently in the environment. The form of nutrient (i.e., inorganic versus organic or dissolved versus particulate) delivered by groundwater may control the biological effect in the receiving coastal marine ecosystem (Seitzinger et al., 2002a). Inorganic nutrients are bioavailable and therefore consumed rapidly by phytoplankton. While organic nutrients may need to be decomposed by bacteria to become bioavailable (Kroeger et al., 2006), there is increasing evidence that algae and higher plants can directly take up organic nutrients (Bronk et al., 2007; Volkmann et al., 2016). Recent studies showed that groundwater-derived dissolved nutrient inputs have a substantial influence on primary productivity and alter the composition of phytoplankton in coastal areas (Zhang et al., 2016; Rodellas et al. 2015). However, the relative importance of organic nutrient vs. inorganic nutrient is not well understood in a SGD context.

Since coastal groundwater nutrient concentrations can be higher than in surface waters, the supply of nutrients through groundwater may influence nitrogen to phosphorus Redfield ratios (Redfield, 1934) and shift surface water typical N-limiting conditions to P-limiting (Slomp and Van Cappellen, 2004). As coastal wetlands and estuaries are drained for development, they may become more groundwater dominated and shift to P-limiting conditions (Santos et al., 2013). The subterranean estuary also plays an important role in the amount of groundwater nutrient input and N:P ratio in coastal waters. This mixing zone is biogeochemically active and can cause rapid changes in nutrient speciation and transformation (Charette and Sholkovitz, 2002). Moreover, because of chemical and biological processes in the subterranean estuary, SGD may have a different composition than the conventional simple mixing between fresh and saline groundwater (Moore et al., 2003). Additional studies in estuarine environments and subterranean estuaries are required to constrain nutrient transformations and the potential effects of nutrient inputs through groundwater discharge on N:P ratios in estuaries.

In this paper, we hypothesize that both fresh and saline SGD play a major role in delivering nutrient to estuary surface waters. We test this hypothesis by performing detailed
measurements of nutrients in a tidal estuary and subterranean estuary. Our objectives were to (1) estimate surface water nutrient export from the mouth of the estuary to coastal waters under contrasting hydrological conditions (wet and dry season), (2) quantify the relative importance of meteoric deep fresh, and shallow saline groundwater-derived nutrient inputs to the estuary, and (3) determine the relative importance of groundwater in the total nutrient exports from the estuary to the coastal ocean. This paper builds on the literature by investigating the contribution of deep fresh groundwater discharge versus shallow saline groundwater discharge in the transport and transformation of nutrients in estuaries as well as investigating how groundwater may alter N:P ratios and the release of organic nutrients in surface waters. We rely on a radium mass balance reported in a companion paper to separate the fluxes of fresh and saline groundwater (Sadat-Noori et al., 2015).

4.2 Material and methods

4.2.1 Study site

Field measurements were conducted at Korogoro Creek (latitude 31.04781°, longitude 153.06492°), a small subtropical tidal estuary in New South Wales, Australia (Figure 4.1A). The estuary is ~5 km long, ~20–25 m wide, has an average depth 0.9 m, and a high tide surface area of ~116×10^3 m^2. The estuary catchment size is 18 km^2 and is characterized by a low topography which is subject to flooding by seawater during spring tides. The estuary has a residence time of around 1 day and is normally flushed during each tidal cycle, with ocean water penetrating the lower 4 km of the estuary at high tide (Ruprecht and Timms 2010). The region has a mild subtropical climate with an average annual rainfall of 1490 mm. The highest (26.9 °C) and lowest (11.2 °C) mean air temperatures are experienced in January and July, respectively, whilst rainfall is highest from February to March (175.2 mm month^-1) and lowest from July to September (71 mm month^-1) (http://www.bom.gov.au). This estuary has been well studied from a hydrological (Acworth et al., 2007; Sadat-Noori et al., 2015) and biogeochemical perspective (Sanders et al., 2015; Sadat-Noori et al., 2016), but nutrient observations have not been reported before.
Two field campaigns were carried out under different hydrological conditions. In the first field campaign there was 375 mm of rain over the preceding month while in the second field campaigns there was 103 mm (Figure 4.1C). Based on the rainfall events in the area, and for simplicity, the first field campaign was termed the wet season and the second the dry season. The wet season field campaign was conducted from 25-27 March, 2013, while the dry season field campaign was carried out from 6-10 June 2013 with both field campaigns being conducted around spring tide.

### 4.2.2 Surface water time series sampling

During both field campaigns, we deployed an automatic high frequency time series monitoring station at the mouth of the estuary. A calibrated Hydrolab automatic logger was used to measure pH (±0.02), salinity (±0.02), dissolved oxygen (±0.2 mg L⁻¹) and water temperature (±0.10 °C), at 15 min intervals during both sampling campaigns. An
acoustic Doppler current profiler (ADCP; Sontek Argonaut) was installed in the middle of the estuary to measure current velocity and direction of flow averaged over 10 min intervals whilst depth loggers (CTD divers; Schlumberger Water Services) measured estuary depth (±0.01 m), at 10 min intervals. These ancillary data as well as radium isotope observations are reported in our companion paper (Sadat-Noori et al. 2015).

Discrete nutrient samples were collected using a sample-rinsed 60 ml polyethylene syringe every hour for about 25 h in both seasons. Samples were filtered through 0.45 μm cellulose acetate filters for later analysis of nitrate + nitrite (hereafter referred to as NO₃), ammonium (NH₄), total dissolved nitrogen (TDN), ortho-phosphate (PO₄) and total dissolved phosphorus (TDP). Samples were stored on ice immediately after sampling until returned to the laboratory where they were stored frozen until analysis.

4.2.3 Groundwater Sampling

During both field campaigns groundwater samples were collected at the same time as surface water sampling was under way. Shallow samples were collected using a push point piezometer system (Charette and Allen 2006) or by digging wells ranging between 0.5 and 2 m deep adjacent to the estuary near the time series station. A 2D-groundwater transect was sampled with bores up to two meters deep and at half a meter increments at low tide (Figure 4.1B). The sampling started at the high tide mark and moved towards the low tide mark. The tubing for sampling was thoroughly flushed with the sample water prior to collecting each sample. A calibrated handheld YSI multiprobe was used to measure pH, temperature, DO, and salinity for each groundwater sample. Nutrient samples were collected as per surface water methods described earlier. Deep (5 to 21 m) monitoring wells installed by the NSW Office of Water located across the catchment were also sampled (Figure 4.1A). A peristaltic pump was used to collect samples after the well volume was purged at least 3 times.

Groundwater discharge into the estuary surface water was divided into shallow saline and deep fresh groundwater components. We used the depth at which the sample was collected as the separating factor rather than salinity as the tidal estuary has a short resident time and therefore salinity may not truly represent the spatial groundwater distribution along the estuary. Additionally, because average radium concentrations were >70-fold higher in samples collected bellow 5 m, the 5 m mark was used as the division point. The average ²²⁴Ra concentration in groundwater at each depth (above and below 5m) was used as the end-
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member and to estimate separate discharge rates for fresh and saline groundwater discharging in each season. We refer to estuarine surface water that recirculates through the sediments as saline groundwater.

4.2.4 Analytical Techniques

Dissolved nutrient analysis (NO\textsubscript{3}, NH\textsubscript{4} and PO\textsubscript{4}) was carried out colourimetrically using a Lachat Flow Injection Analyser. Total dissolved nitrogen and total dissolved phosphorus were determined using the same analysis after digestion with a di-potassium eroxodisulphate solution and the sample was autoclaved. Dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) were determined as the difference between the total dissolved nutrient concentration and the dissolved inorganic concentrations. Analytical errors better than 5% were determined as the average percentage coefficient of variation of triplicate samples. Additional details on method and detection limits can be found in Eyre and Ferguson (2005).

4.2.5 Calculations

The estuarine export (ebb tide) and import (flood tide) of nutrients were estimated by multiplying hourly surface water discharge rates by nutrient concentrations in surface waters, and then integrating hourly fluxes from high to low tide (or low to high tide). Hourly surface water discharge rates were calculated based on specific cross sectional area (adjusted for tidal height) and measured current velocity assuming homogenous currents across the channel. Fresh and saline groundwater-derived nutrient fluxes were calculated by multiplying groundwater fluxes estimated from a radium mass balance (Sadat-Noori et al. 2015) and the median groundwater nutrient concentration. \textsuperscript{224}Ra was used due to the largest concentration difference in fresh and saline groundwater samples which significantly assists in distinguishing the two sources. \textsuperscript{224}Ra also has a half-life of 3.6 days which is on the same temporal scale as physical processes that drive estuarine mixing and tidally-driven groundwater discharge. Briefly, the non-steady state radium mass balance model accounted for all known sources and sinks of radium entering and leaving the system over a 24 h diel cycle. Inputs to the radium model were groundwater, upstream \textsuperscript{224}Ra input flux during flood tide, diffusion from sediments, and desorption from suspended sediments while outputs consisted of \textsuperscript{224}Ra downstream flux during ebb tides and the decay. Daily averages where calculated by integrating export and
import rates over two tidal cycles then dividing by total time for the two tidal cycles (~25 h) to get an hourly rate, and multiplying by 24 (hours in 1 day) to estimate a daily rate. The median groundwater nutrient concentration was used due to the non-normal distribution of the groundwater endmember concentrations. Uncertainty for export rates were calculated based on the basic rules of error propagation. Standard errors are reported for concentration uncertainties.

## 4.3 Results

### 4.3.1 Surface water

Salinity followed a similar tidal trend in both seasons and ranged from 7.4 to 34.7 in the wet season and from 3.9 to 35.8 in the dry season over the 24 h time series sampling at the mouth of the estuary (Figure 4.2). Radium-224 also followed a tidal trend in both seasons with the lowest concentrations being recorded at high tide. The average radium-224 concentration was $46.0 \pm 6.1$ and $39.3 \pm 3.9$ dpm 100L$^{-1}$ ($\pm$SE) in the wet and dry seasons respectively (Figure 4.2; Table 4.1). Surface water nutrient concentrations followed a distinct tidal pattern with the highest concentrations observed at low tide. The median surface water NO$_3$ concentrations were 0.42 and 0.62 µmol L$^{-1}$ in the wet and dry seasons, respectively. The range of NH$_4$ concentrations was larger in the wet (0.68 – 6.50 µmol L$^{-1}$) than the dry season (0 – 4.94 µmol L$^{-1}$). Median DON concentrations were 17.93 and 30.62 µmol L$^{-1}$ in wet and dry season, respectively. PO$_4$ concentrations ranged from 0.15 to 0.81 µmol L$^{-1}$ in the wet season and 0.17 to 0.43 µmol L$^{-1}$ in the dry season. DOP concentrations were similar in wet and dry season (0.35 and 0.32 µmol L$^{-1}$, respectively). TDN and TDP median concentrations were 1.8 and 1 fold higher in the dry season than the wet, respectively (Table 4.2).

<table>
<thead>
<tr>
<th>Hydrological variables</th>
<th>Wet Season</th>
<th>Dry Season</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salinity range</td>
<td>7.4 – 34.7</td>
<td>3.9 – 37.8</td>
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<tr>
<td>Rainfall (mm) - over preceding month</td>
<td>375</td>
<td>103</td>
</tr>
<tr>
<td>Surface water discharge (m$^3$ s$^{-1}$)</td>
<td>3.0</td>
<td>2.3</td>
</tr>
<tr>
<td>Fresh GW discharge (m$^3$ s$^{-1}$)</td>
<td>0.71±0.25</td>
<td>0.04±0.01</td>
</tr>
<tr>
<td>Saline GW discharge (m$^3$ s$^{-1}$)</td>
<td>0.33±0.09</td>
<td>0.19±0.23</td>
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</table>
Figure 4. 2 Surface water depth (m), salinity, nutrient concentration (µmol L$^{-1}$) and radium (dpm 100L$^{-1}$) time series at Hat Head Estuary, during the wet and dry seasons. Ancillary data originally reported in Sadat-Noori et al. (2015).
NO₃ export rates in the wet season were 7 ± 2 µmol m⁻² catchment d⁻¹ and 5 ± 1 µmol m⁻² catchment d⁻¹ in the dry season. NH₄ export from estuary in the wet season (54 ± 11 µmol catchment m⁻² d⁻¹) was 3 fold higher than in dry season (18 ± 4 µmol catchment m⁻² d⁻¹). PO₄ export rates (3 ± 1 µmol m⁻² catchment d⁻¹) were similar in both season. DON, DOP, TDN and TDP exports were 120%, 45%, 56% and 36% higher in the wet season compared to the dry season (Table 4.2).

For both flood and ebb tides, DON was the dominant form of nitrogen (~88% flood and ~86% ebb), however during the wet season, the total TDN pool was 2 fold higher than the dry (Figure 4.3). Ebb tide TDN export in the wet season (486 µmol m⁻² catchment d⁻¹) was 1.6-fold higher than ebb tide TDN export in the dry season (293 µmol m⁻² catchment d⁻¹) while TDN import from flood tides were higher in the dry season. The major form of nitrogen in groundwater and surface water in both seasons was DON. In the wet season fresh groundwater NO₃ inputs to estuary exceed estuary export rates indicating a loss possibly due to denitrification along the estuary mixing gradient.

![Figure 4.3](image_url)

**Figure 4.3** Pie charts showing the relative contribution of the different nitrogen species to the TDN pool in surface and groundwater in wet and dry seasons. Flood and ebb pie chart are based on export rates. TDN import and export rates are in units of µmol m⁻² catchment d⁻¹.
Table 4.2 Surface water nutrient concentrations, estuary-wide and catchment nutrient export. Uncertainty was calculated following on the basic rules of error propagation.

<table>
<thead>
<tr>
<th></th>
<th>Wet</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Median Conc. (µmol L⁻¹)</td>
<td>Surface water export from estuary (µmol m² estuary d⁻¹)</td>
<td>Surface water export from catchment (µmol m² catchment d⁻¹)</td>
<td>Median Conc. (µmol L⁻¹)</td>
<td>Surface water export (µmol m² estuary d⁻¹)</td>
<td>Surface water export from catchment (µmol m² catchment d⁻¹)</td>
<td>Surface water export (µmol m² estuary d⁻¹)</td>
<td>Surface water export from catchment (µmol m² catchment d⁻¹)</td>
<td>Surface water export (µmol m² estuary d⁻¹)</td>
<td>Surface water export from catchment (µmol m² catchment d⁻¹)</td>
</tr>
<tr>
<td>NO₃</td>
<td>0.42</td>
<td>1053±211</td>
<td>7±2</td>
<td>0.62</td>
<td>758±152</td>
<td>5±1</td>
<td>905±182</td>
<td>6±1</td>
<td>5568±1114</td>
<td>36±7</td>
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<td>NH₄</td>
<td>3.08</td>
<td>8395±1679</td>
<td>54±11</td>
<td>3.15</td>
<td>2741±548</td>
<td>18±4</td>
<td>5568±1114</td>
<td>36±7</td>
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<td>DON</td>
<td>17.93</td>
<td>55479±11096</td>
<td>358±72</td>
<td>30.62</td>
<td>2502±5005</td>
<td>161±32</td>
<td>46726±9345</td>
<td>302±60</td>
<td>46726±9345</td>
<td>302±60</td>
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<tr>
<td>TDN</td>
<td>19.57</td>
<td>64927±12985</td>
<td>419±84</td>
<td>35.75</td>
<td>28525±5705</td>
<td>184±37</td>
<td>46726±9345</td>
<td>302±60</td>
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<td>302±60</td>
</tr>
<tr>
<td>PO₄</td>
<td>0.20</td>
<td>490±98</td>
<td>3±1</td>
<td>0.31</td>
<td>399±79</td>
<td>3±1</td>
<td>443±89</td>
<td>3±1</td>
<td>443±89</td>
<td>3±1</td>
</tr>
<tr>
<td>DOP</td>
<td>0.35</td>
<td>871±174</td>
<td>6±1</td>
<td>0.32</td>
<td>473±94</td>
<td>3±1</td>
<td>672±134</td>
<td>4±1</td>
<td>672±134</td>
<td>4±1</td>
</tr>
<tr>
<td>TDP</td>
<td>0.55</td>
<td>1361±272</td>
<td>9±2</td>
<td>0.63</td>
<td>868±174</td>
<td>6±1</td>
<td>1115±223</td>
<td>7±2</td>
<td>1115±223</td>
<td>7±2</td>
</tr>
</tbody>
</table>

Note that TDN may not exactly equal DIN+DON as median values are used.
4.3.2 Groundwater

In the wet season, the input of fresh deep groundwater-derived NO$_3$ (3001.4 ± 3001.4 µmol m$^{-2}$ of estuary d$^{-1}$) and NH$_4$ (3687.1 ± 3687.1 µmol m$^{-2}$ estuary d$^{-1}$) was 70 and ~3 times higher than saline shallow groundwater-derived NO$_3$ (43.7 ± 9.7 µmol m$^{-2}$ estuary d$^{-1}$) and NH$_4$ (1360.4 ± 316.5 µmol m$^{-2}$ estuary d$^{-1}$) (Table 4.2). DON derived from fresh deep groundwater was ~25 fold higher than saline shallow groundwater. The flux of fresh and saline groundwater-derived PO$_4$ was 180.0 ± 180.0 and 271.0 ± 56.1 µmol m$^{-2}$ estuary d$^{-1}$, respectively. Groundwater-derived DOP flux from fresh groundwater was ~7 fold higher than saline groundwater-derived DOP.

In the dry season, groundwater-derived NO$_3$ flux from fresh and saline groundwater sources were similar (148.0 ± 328.0 and 100.5 ± 123.8 µmol m$^{-2}$ estuary d$^{-1}$, respectively) while the flux of NH$_4$, DON, PO$_4$ and DOP from saline groundwater was approximately 7, 14, 10, and 2 fold higher than the fresh groundwater fluxes. In general nutrient fluxes from fresh groundwater were higher in wet season while in the dry season groundwater-derived nutrients fluxes from saline groundwater were dominant (Table 4.3).
Table 4.3 Groundwater-derived nutrient fluxes based on the area of the estuary (µmol m\(^{-2}\) estuary d\(^{-1}\)). Fresh and saline groundwater discharge rates were calculated using a radium mass balance as described in Sadat-Noori et al. (2015). Uncertainty was calculated following the basic rules of error propagation.

<table>
<thead>
<tr>
<th></th>
<th>Wet Median Conc. (µmol L(^{-1}))</th>
<th>GW input (µmol m(^{-2}) estuary d(^{-1}))</th>
<th>Dry Median Conc. (µmol L(^{-1}))</th>
<th>GW input (µmol m(^{-2}) estuary d(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Saline</td>
<td></td>
<td>Fresh</td>
<td></td>
</tr>
<tr>
<td>SGD (m(^3) s(^{-1}))</td>
<td>0.33±0.09</td>
<td></td>
<td>0.19±0.23</td>
<td></td>
</tr>
<tr>
<td>NO(_3)</td>
<td>0.18±1.28</td>
<td>43.7±9.7</td>
<td>0.71±0.87</td>
<td>100.5±123.8</td>
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<tr>
<td>NH(_4)</td>
<td>5.54±0.85</td>
<td>1360.4±316.5</td>
<td>8.46±6.13</td>
<td>1195.1±1110.3</td>
</tr>
<tr>
<td>DON</td>
<td>11.49±0.97</td>
<td>516.6±109.7</td>
<td>62.85±26.46</td>
<td>8881.8±8024.4</td>
</tr>
<tr>
<td>TDN</td>
<td>18.30±1.74</td>
<td>4492.6±965.4</td>
<td>66.48±31.83</td>
<td>9395.3±8487.9</td>
</tr>
<tr>
<td>PO(_4)</td>
<td>1.10±0.06</td>
<td>271.0±56.1</td>
<td>0.62±0.73</td>
<td>88.3±80.9</td>
</tr>
<tr>
<td>DOP</td>
<td>0.15±0.05</td>
<td>38.0±11.3</td>
<td>0.20±0.16</td>
<td>28.8±31.6</td>
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<td>TDP</td>
<td>1.21±0.08</td>
<td>296.6±61.8</td>
<td>0.53±0.47</td>
<td>74.8±587.4</td>
</tr>
<tr>
<td></td>
<td>Fresh</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>SGD (m(^3) s(^{-1}))</td>
<td>0.71±0.25</td>
<td></td>
<td>0.04±0.01</td>
<td></td>
</tr>
<tr>
<td>NO(_3)</td>
<td>5.68±2.07</td>
<td>3001.4±3001.4</td>
<td>5.68±2.07</td>
<td>148.0±328.0</td>
</tr>
<tr>
<td>NH(_4)</td>
<td>6.98±4.98</td>
<td>3687.1±3687.1</td>
<td>6.98±4.98</td>
<td>181.8±112.0</td>
</tr>
<tr>
<td>DON</td>
<td>23.98±13.61</td>
<td>12663.7±12663.7</td>
<td>23.98±13.61</td>
<td>624.3±493.4</td>
</tr>
<tr>
<td>TDN</td>
<td>55.17±38.77</td>
<td>29135.5±29135.5</td>
<td>55.17±38.77</td>
<td>5984.8±3300.2</td>
</tr>
<tr>
<td>PO(_4)</td>
<td>0.34±0.48</td>
<td>180.0±180.0</td>
<td>0.34±0.48</td>
<td>8.9±35.4</td>
</tr>
<tr>
<td>DOP</td>
<td>0.47±0.19</td>
<td>250.4±250.4</td>
<td>0.47±0.19</td>
<td>12.3±9.8</td>
</tr>
<tr>
<td>TDP</td>
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<td>1.24±1.47</td>
<td>134.3±526.4</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SGD (m(^3) s(^{-1}))</td>
<td>1.0±0.3</td>
<td></td>
<td>0.2±0.2</td>
<td></td>
</tr>
<tr>
<td>NO(_3)</td>
<td>3045.1±743.8</td>
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<td>248.4±61.1</td>
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<tr>
<td>NH(_4)</td>
<td>5047.5±3204.6</td>
<td></td>
<td>1376.9±338.9</td>
<td></td>
</tr>
<tr>
<td>DON</td>
<td>13180.3±5498.7</td>
<td></td>
<td>9506.1±2339.9</td>
<td></td>
</tr>
<tr>
<td>TDN</td>
<td>33628.1±8948.5</td>
<td></td>
<td>15380.2±3785.9</td>
<td></td>
</tr>
<tr>
<td>PO(_4)</td>
<td>451.0±740.5</td>
<td></td>
<td>97.2±23.9</td>
<td></td>
</tr>
<tr>
<td>DOP</td>
<td>288.4±182.8</td>
<td></td>
<td>41.2±10.1</td>
<td></td>
</tr>
<tr>
<td>TDP</td>
<td>950.6±2591.5</td>
<td></td>
<td>209.1±24.6</td>
<td></td>
</tr>
</tbody>
</table>

Estuary area 116,160 m\(^2\); catchment area 18 km\(^2\).

Within the subterranean estuary deeper anoxic and brackish groundwater contained the highest ammonium concentrations (Figure 4.4). Surface nitrate was higher than deeper samples, and higher nitrate concentrations corresponded to a small oxic area irrespective of whether these samples were saline or fresh. A high concentration DON plume was observed a
meter beneath the surface directly on top of the ammonium plume. DOP concentrations were slightly higher in the samples close to surface (Figure 4.4).

**Figure 4.4** A groundwater 2D nutrient transect sampled in the wet season at low tide.

### 4.3.3 Nitrogen to phosphorus ratios

The ratio of nitrogen to phosphorus is an important factor controlling phytoplankton production and community composition in estuarine environments. Phytoplankton typically utilise N:P in the ratio of 16:1 (Redfield, 1934). In the wet season, groundwater DIN:DIP was below the Redfield ratio. However, when both inorganic and organic forms are taken into
account, the ratio falls largely around the Redfield ratio (Figure 4.5). In the dry season groundwater is above Redfield ratio, calculated with both DIN:DIP and TDN:TDP. Surface water samples show clear P-limiting conditions in both seasons using either inorganic or total forms of nutrients. The average TDN:TDP ratio in Hat Head estuary surface and groundwater was 47.5 and 50.1, respectively showing P-limiting conditions. However, if only the inorganic form of nitrogen is considered, the DIN:DIP ratio would change significantly, reducing to 14.8 and 18.7 for surface and groundwater.

Figure 4. 5 Groundwater and surface water DIN:DIP and TDN:TDP plots in wet and dry seasons. The dashed line indicates the Redfield Ratio.

4.4 Discussion

4.4.1 Surface water nutrient exports

Surface water nutrient fluxes indicated that the estuary was a source of nutrients to the coastal waters in both wet and dry study periods. Higher exports rates of total dissolved
nitrogen and phosphorus were observed in the wet season despite higher surface water concentrations in the dry season (Table 4.2). Averaged over the entire year, DIN export from the catchment was 15.3 mmol m⁻² catchment yr⁻¹. Modelled global DIN export to the coastal ocean by rivers is reported to be 236×10⁹ mol yr⁻¹ (Mayorga et al., 2010). Using the total land drainage area of all continents of 114×10⁶ km² (Beusen et al. 2005; Seitzinger et al., 2002b), global riverine DIN exports per unit area to coastal waters would be 2.0 mmol m⁻² yr⁻¹ which is 7-fold lower than the DIN export observed during this study. On the continental scale, Australia DIN export from rivers to the coastal waters is estimated to be 25×10⁸ mol yr⁻¹ (Seitzinger et al., 2002b). Considering Australia’s exoreic surface area (5.5 million km²; Harrison et al., 2005), Australian DIN exports rates would be 0.45 mmol m⁻² yr⁻¹ or 30 times less than the DIN export seen in this study. The reason for this high DIN export is likely due to the combination of the fertile coastal floodplain, surrounding agriculture lands, wetlands, porous sediments that could allow for significant volumes of high nutrient groundwater into the estuary, and short estuarine residence time preventing significant nutrient consumption. Wetlands are natural ecosystems that gather, transform and export inflowing nutrient-rich waters (Sánchez-Carrillo et al., 2009). Previous studies have shown wetlands to have DIN export rates of 21 mmol m⁻² yr⁻¹ (Santos et al., 2013) and 165 mmol m⁻² yr⁻¹ (Kovacic et al., 2000). As more than 70% of the Hat Head estuary catchment is wetlands, this could likely be a significant source of the high DIN export.

Hat Head estuary surface water DIP export (1.09 mmol m⁻² catchment yr⁻¹) was >2-fold higher than the global exoreic DIP export per unit area to coastal waters delivered by rivers which is reported to be 0.46 mmol m⁻² yr⁻¹ (Mayorga et al., 2010). Surface water DIP exports from this study were approximately 21-fold greater than the DIP export rates from the Australian continent (0.05 mmol m⁻² yr⁻¹) (Mayorga et al., 2010, Seitzinger et al., 2005). Therefore, our observations indicate the Hat Head’s small catchment disproportionally contribute, to nutrient exports to the nearby ocean.

4.4.2 Groundwater-derived nutrient inputs: Fresh vs Saline

Groundwater was shown to be an import pathway for nitrogen and phosphorous to surface waters in Hat Heat estuary. Groundwater-derived DIN from Hat Head estuary ranged from 1.6 to 8.1 mmol m⁻² estuary d⁻¹ in dry and wet season, respectively. To put the results in perspective, we compare Hat Head with a number of studies conducted over a range of scales. Santos et al., (2008) reported similar GW-derived DIN fluxes of 6 mmol m⁻² d⁻¹ from
a non-contaminated coastal plain in the Gulf of Mexico. Boehm et al. (2004) estimated GW-derived DIN fluxes of 0.7 to 12 mmol m$^{-2}$ d$^{-1}$ in coastal open waters located at Huntington Beach, USA. Hwang et al. (2005) reported higher fluxes of 21.4 mmol m$^{-2}$ d$^{-1}$ driven by high SGD rates from Bangdu Bay on Jeju Island, Korea. In smaller estuarine systems, lower GW-derived DIN fluxes of 0.33 mmol m$^{-2}$ d$^{-1}$ were estimated from Pettaquamscutt Estuary, USA, likely due to a smaller groundwater nutrient reservoir in the region (Kelly and Moran, 2002) while average SGD-derived NO$_3$ flux from Werribee Estuary, Australia was reported to be 166 mmol m$^{-2}$ d$^{-1}$, 35 fold higher than our average observations (Wong, et al. 2013).

In the Hat Head estuary, the dominant form of nitrogen exported via groundwater was DON, followed by NH$_4$ and NO$_3$ from fresh groundwater, in the wet season (Table 4.3). Average total groundwater fluxes of NO$_3$, PO$_4$, NH$_4$, DON, DOP, TDN and TDP were estimated to account for 66, 58, 55, 31, 21, 53 and 47 % of surface water exports, respectively (Figure 4.6). This demonstrates that groundwater can be a major source of nutrients from small estuaries to the coastal waters. The positive relationship observed between radium and nutrient species provides evidence that is consistent with the mass balance in indicating a major contribution of groundwater in delivering nutrients to the estuary (Figure 4.7). Previous studies have also indicated that groundwater discharge plays an important role in delivering DIN to estuaries (Moore, 2006; Wong, et al. 2013; Porubsky et al., 2014). In a study in the upper Gulf of Thailand, groundwater-derived DIN, DIP, DON and DOP were reported to be 40-50%, 60-70%, 30-40% and 30-130% of the fluxes delivered by the Chao Phraya River into the ocean (Burnett et al., 2007). The contribution of groundwater to surface water exports increased from 4% in the wet season to 20% in the dry season (Dulaiova et al., 2006).
Figure 4.6 The contribution of groundwater-derived nutrient to total estuary nutrient export in wet and dry seasons (upper plots), and export rates for estuary surface water, fresh GW and saline GW in both seasons (lower plots). Note that export scale is in log scale.
Figure 4.7 Surface water radium-224 and salinity vs nutrient concentrations and N:P ratios. The lines on the salinity mixing plots represent the theoretical conservative mixing line.
The relative contribution of fresh groundwater-driven nutrient export to estuary waters was highest in the wet season. This was largely due to the higher proportion of groundwater discharge from deep fresh sources in the wet season (Table 4.1). The higher groundwater levels during the wet season increased hydraulic head, and consequently the hydraulic gradient, which in turn would drive higher SGD fluxes (Sadat-Noori et al., 2015). In the wet season, TDN from fresh terrestrial groundwater was the main contributor (~45% of the total 52% groundwater contribution) to total TDN export from the estuary. This however changed in the dry season and saline groundwater became the dominant source of TDN (33% of the total 54% groundwater contribution) (Figure 4.6). This significant contribution of saline groundwater is in contrast with findings from Weinstein et al. (2011) which indicated that the recirculated seawater component of SGD can often be relatively nutrient-poor. However, a study conducted in a Florida coastal bay, suggested significant loads of nitrogen were delivered via recirculated saline groundwater (Kroeger et al., 2007). Similarly, in a study from the north-eastern Gulf of Mexico, saline porewater was reported to contain high loads of nutrients, with the source being mineralization of marine organic matter within the subterranean estuary (Santos et al., 2009). Here, the major driver of fresh groundwater nutrient in the wet season was likely increased flux rates of SGD from increased hydraulic gradient which has the capacity to deliver deep, nutrient rich groundwaters into the estuary. In the dry season where the hydraulic head was lower, tidal pumping of recirculated seawater was the dominant groundwater nutrient source.

There are some limitations regarding our sampling strategy. We were not able to collect deep groundwater samples during the wet season, due to flooding of the overlying catchment. However, previous studies have indicated that deep groundwater has relatively stable temporal composition (Dhar et al. 2008; Santos et al., 2009; Chapagain et al. 2010), and therefore we assumed that the dry season deep groundwater concentrations were representative of wet season concentrations. In order to account for this, we have assigned a 100% uncertainty to the estimated deep GW fluxes in the wet season when propagating errors in fluxes (Table 4.3). Another limitation regarding our GW-derived nutrient fluxes is that we only have data from two field campaigns. Additional sampling incorporating seasonal and annual temperature differences, different terrestrially nutrient loading, and the impacts of floods on local hydrology and nutrient dynamics could also influence exports rates (Constantz et al., 1994; de Sieyes et al., 2008).
4.4.3 Nutrient dynamics in surface and groundwater

Nutrient speciation may change as deeper groundwater moves to surface waters (Knee et al., 2008). Surface water salinity mixing plots showed that in the wet season, NH$_4$ had a convex trend indicating production while NO$_3$ illustrated a concave trend relative to the theoretical conservative mixing line indicating consumption occurring as mixing of seawater and fresh water takes place (Figure 4.7). In the dry season, conservative mixing was observed for NH$_4$ and NO$_3$ possibly due to cooler temperatures which reduce primary productivity and microbial respiration rates (Maher and Eyre 2011). The nitrate-consumption process may be caused by denitrification or dissimilatory nitrate reduction to ammonium (DNRA) (Gardner et al., 2006; Tait et al., 2014). Denitrification seems more likely due to the high nitrate and organic matter supply in Hat Head estuary. Other sources of nutrient that could account for the remaining extra nitrogen export from the estuary (difference between import at high tide and export at low tide) may be surface water runoff, nitrogen fixation or resuspension. Phosphate showed conservative mixing in the wet season while production was seen in the dry season similar to DOP (Figure 4.7).

Groundwater nutrient salinity mixing plots did not show simple trends which may be masked by the spatial variability in GW nutrient concentration (Figure 4.8) as observed before (Santos et al., 2009). However, the 2D transect observations shows much clearer trends (Figure 4.4). As deep NH$_4$ laden groundwater, moves through the subterranean estuary (the brackish zone) to the surface, it undergoes nitrification to NO$_3$ when sufficient dissolved oxygen is available. At this point of nitrification, there is also significant DON production arising from the breakdown of microbial matter. This may partially explain the large DON exports from the estuary. As estuarine waters are recirculated through sediments, the produced NO$_3$ and DON would be discharged into the surface waters. Similar subterranean estuary dynamics were observed by Kroeger et al., (2008) and Erler et al., (2014) where local organic matter produced NH$_4$ in the deeper anoxic groundwater and a NO$_3$ rich brackish water plume was located in shallow groundwaters a meter below the surface. Erler et al. (2014) also used N isotopes to show that the loss of NH$_4$ through nitrification increased towards the surface and reduced NH$_4$ concentrations by up to 80%.
Figure 4.8 Groundwater nutrients concentration and N:P ratios vs salinity scatter plots.
Previous studies have suggested that DON may be enriched in groundwater relative to surface waters (Kim et al., 2013; Santos et al., 2013; Santos et al., 2014). Here, groundwater nitrogen was dominated by DON, accounting for 66 and 85% of TDN in groundwater in the wet and dry season, respectively. The fraction of DON in surface water was ~88% of TDN in both the wet and dry seasons. The reason for the high DON concentrations observed in surface waters is likely due to DON-rich groundwater inputs as supported by the positive correlation between radium-224 and DON concentrations (Figure 4.7). Additionally, the production of DON in the mid subterranean estuary delivered by both fresh and recirculated groundwater sources contributes to high DON concentrations.

4.4.4 N:P ratios

Average TDN:TDP ratio in the dry season was 144 ± 35 (SE) in saline groundwaters indicating P-limited conditions while it was 16 ± 1 (SE) in the fresh groundwaters. This shows the potential role saline groundwater can play in shifting N:P ratios. Surface water N:P ratios indicated that when organic nutrients are included, the estuary is P-limited on both ebb and flood tide however not at low tide (Figure 4.9). Alternatively, when ratios are calculated using only inorganic nutrients, the estuary was P-limited during flood tides and N-limited on ebb tides during the wet season. In the dry season, surface water was N-limited on both ebb and flood tides but not at direct low tide. This suggests that groundwater discharge of inorganic nitrogen in the wet season (as illustrated in Figure 4.6) may change the estuary to P limitation. The significant correlations between the groundwater tracer $^{224}$Ra and N:P ratios (Figure 4.7) further supports the notion that groundwater discharge can increase the N:P ratios of estuary surface waters providing multiple lines of evidence that groundwater exerts a strong control over surface water nutrient ratios as also observed in a mangrove creek (Gleeson et al., 2013).
Hwang et al., (2005) reported high DIN:DIP ratios (96–193) in groundwater and suggested a large DIN:DIP imbalance can affect the ecosystem of coastal seawater. Santos et al., (2013) showed that a post-flood groundwater seepage in a coastal floodplain can shift the system from a DON to a DIN-dominated system and groundwater inputs doubled the N:P ratio in surface waters. Groundwater discharge was also reported to drive high N:P ratios in two estuaries in New Zealand (Santos et al., 2014). The common conception that TDN loads which have high DIN:DON ratios can create favourable conditions for eutrophication rather
than TDN loads with less DIN may not be the case in estuaries. Previous studies have showed that DON uptake can rival DIN in some cases and that DON can play a major role in eutrophication (Bronk et al., 1998; Antia et al., 1991). Some recent studies have suggested that DON provides an alternative to DIN as a nitrogen source that allows the successful growth of macrophytes (Mozdzer et al., 2010; Volkmann et al., 2016).

Previous studies have used either inorganic or total dissolved forms of nutrient to calculate N:P ratios (Santos et al., 2014, Slomp and Van Cappellen, 2004) with little discussion on whether N:P ratios should be based on inorganic or total nutrients. For example TDN:TDP may be preferred over DIN:DIP for calculating N:P ratios as total concentrations provide analytically robust estimates of bioavailable N and P, and TDN is considered the analogue of TDP and its use (Zirino et al., 2016; Lomas et al., 2009). Other studies have used DIN:DIP ratios (Kim et al., 2003; Murrel et al., 2007; Wang et al., 2015). Here significantly lower N:P ratios were observed when only inorganic nutrients were used to calculate N:P ratios. Therefore, not including organic nutrient in N:P ratios may lead to an underestimation in the potential limitation of primary production by nitrogen. Moreover, the groundwater-derived DON dominates the estuaries surface water at ebb tide in both wet and dry conditions (Figure 4.3), and some portion of particulate phosphorus in the estuary can become bioavailable. Both processes drive high productivity, suggesting TDN:TDP is a more useful index for calculating N:P ratios in the estuary investigated.

4.5 Conclusions

We estimated both fresh terrestrial groundwater and saline groundwater nutrient fluxes into a tidal estuary and the relative contribution of groundwater to surface water exports to the coastal ocean. Average nutrient fluxes over the study period showed that the estuary was a source of nutrient to the coastal waters. DIN exports were 7-fold higher than the global flux rate estimate for rivers and 30 times more than Australian surface water averages. Groundwater discharge accounted for up to 53% of TDN and 47% of TDP export from the estuary to the coastal waters. Fresh groundwater accounted for 45% of the TDN and 48% of the TDP export and was the dominant source of nutrient in the wet season while saline groundwater accounted for 32% of TDN export in the dry season. High fluxes of groundwater nitrogen were found to be a major regulator of the observed N:P ratios.

Groundwater entering estuarine surface waters can significantly affect the chemistry and biology of the surface water over short time scales creating a highly dynamic aquatic system.
Phytoplankton’s are important primary producers in coastal waters that can respond rapidly to changes in the environment. Here we show groundwater has the ability to deliver large amount of both inorganic and organic nutrients to estuarine waters. Since coastal phytoplankton community composition is often moderated by DIN availability, groundwater can play a key role in potential shifts in phytoplankton community in estuaries and the nearby coastal ocean. Our observations imply that strategies to manage eutrophication on coastal waters scale should address both groundwater and surface water sources. Small groundwater dominated estuaries can export significantly more nutrients per unit area than larger river systems.
Chapter 5

Intermittently Closed and Open Lakes and/or Lagoons (ICOLLs) as groundwater-dominated coastal systems: Evidence from seasonal radon observations

Chapter 5 | Intermittently Closed and Open Lakes and/or Lagoons (ICOLLs) as groundwater-dominated coastal systems: Evidence from seasonal radon observations

Abstract

Intermittently Closed and Open Lakes or Lagoons (ICOLLs) are dynamic coastal systems that may be vulnerable to changes in catchment hydrology. However, little is known regarding the role of groundwater on the hydrological cycles of ICOLLs. Groundwater discharge in two ICOLLs (Welsby and Mermaid) and a nearby wetland (South Welsby Lagoon) located on Bribie Island (Australia) was quantified using radon ($^{222}$Rn, a natural geochemical groundwater tracer) from observations made during four seasonal surveys. The distribution of radon revealed temporal and spatial changes over the study period with higher surface water radon concentrations found in winter for Welsby ICOLL and in autumn for Mermaid ICOLL. The average estimated groundwater discharge rates from a radon mass balance were 3.4±2.1, 7.3±8.9 and 2.6±1.1 cm d$^{-1}$ in Welsby, South Welsby and Mermaid Lagoons, respectively. These values are at least 8-fold greater than the average annual precipitation that falls directly over the ICOLLs (1420 mm per year, or 0.4 cm d$^{-1}$), which, coupled with minimal surface water runoff due to the permeable sandy soils, demonstrates that these systems are groundwater-dominated. Overall, groundwater discharge rates in these ICOLLs was much larger than has been reported in other lake systems which is most likely due to the high permeability of regional sandy soils and their large shoreline to volume ratio.

Keywords: Submarine groundwater discharge, groundwater hydrology, permeable sediments, coastal lagoon, sand island, coastal wetland.
5.1 Introduction

Intermittently Closed and Open Lakes and Lagoons (ICOLLs) are brackish coastal water bodies with a connection to the ocean that is closed periodically due to the accumulation of marine sediment forming an entrance berm (Haines, 2006). Such systems may also be referred to as semi-permanently closed estuaries, temporarily open–closed estuaries, or simply, coastal lagoons in different parts of the world (Haines et al., 2006). ICOLLs are characterised by intermittent surface water inflows and the opening of ICOLLs usually occurs shortly after periods of high rainfall. ICOLLs are found in many parts of the world including Australia, New Zealand, South Africa, South America and South-western parts of India and Sri Lanka (Hadwen, 2006). In Australia, ICOLLs are mostly located along the southeast coast extending from southern Queensland to the east coast of Victoria, of which approximately 70% are completely enclosed embayments (Ranasinghe and Pattiaratchi, 2003).

ICOLLs have distinctive physical, chemical and biological characteristics. Their shallow nature (typically <5 m) results in a high sediment surface area to water volume ratio, which increases the relative importance of sediment–water column interactions (Tyler et al. 2001). In some cases, where the ICOLL basin is elevated, opening of the entrance berm may completely drain the ICOLL (Schallenberg et al., 2010). Salinity in these systems can vary significantly, from fresh to brackish to hypersaline, depending upon the amount of freshwater input, the climate and the frequency and duration of entrance opening (Ridden and Adams, 2008). Since ICOLLs can act as an accumulation basin and are flushed only periodically, they can be vulnerable to anthropogenic activities, and are considered among the most sensitive estuary type to anthropogenic disturbance (Haines, 2006; Boyd et al. 1992). They are often perceived as a surface expression of shallow aquifers and are thought to be fed by groundwater seepage during most of the year (Chikita et al., 2015) and as such they may be vulnerable to minor changes in catchment and groundwater hydrology. However, our knowledge about the relative contribution of groundwater seepage to ICOLL water budgets remains very limited.

Most previous studies on ICOLLs have focused on the influence of surface water inputs (Chikita et al., 2015, Morris and Turner, 2011). Surface water contributions to the total water budget of ICOLLs can be minimal although can be influenced by a range of factors including sediment permeability. The lack of previous groundwater studies in ICOLLs may be as a result of the inherent difficulty in quantifying groundwater seepage due to the patchy, diffuse, and temporally variable nature of groundwater discharge (Santos et al. 2008). Attempts to
resolve a nutrient mass balance in an ICOLL in South Africa were hindered by lack of data on groundwater discharging into the ICOLL (Human et al., 2015). Similarly, the nutrient loads into two ICOLLs in New Zealand were likely underestimated because the groundwater discharge was not included (Schallenberg et al., 2010). In order to advance our understanding of ICOLL hydrology and biogeochemistry, it is therefore necessary to quantify the role of groundwater discharge to ICOLL water budgets.

Natural geochemical tracers such as radon ($^{222}$Rn) are increasingly being used to quantify groundwater discharge and investigate its effect on water budgets and water quality (Schubert et al., 2011). The main advantage of using natural geochemical tracers is that they integrate different groundwater pathways, which is useful in spatially heterogeneous and temporally dynamic systems (Stiegitz et al., 2010, Burnett et al., 2006). Radon normally occurs in higher concentrations in groundwater relative to surface water, and the decay rate of the radon (half-life = 3.8 days) is on the same temporal scale as many of the physical processes related to groundwater discharge (Burnett et al., 2008). By assessing $^{222}$Rn concentrations in groundwater and the water column, it is possible to estimate the amount of groundwater discharge to coastal surface waters. This is often achieved by mass balance approaches, originally introduced by Cable et al. (1996) and refined by multiple authors over the years (Burnett and Dulaiova, 2003; Santos et al., 2010; Burnett et al., 2010; Tait et al., 2013; Sadat-Noori et al., 2015). However, using a $^{222}$Rn mass balance approach to estimate groundwater fluxes has yet to be attempted in an ICOLL system.

This study uses a radon mass balance to quantify groundwater discharge into two ICOLLs (and a nearby wetland) on Bribie Island, Australia. We hypothesize that groundwater plays a major role in the hydrology of the ICOLLs. To determine the importance of groundwater in these systems, we mapped the groundwater discharge points of entry into the ICOLLs using $^{222}$Rn, and quantified the groundwater discharge into the ICOLLs over four seasons.

5.2 Methods

5.2.1 Site Description

Bribie Island (27.00°S; 153.12°E) is a large sand barrier island, located off the south east coast of Queensland, Australia (Figure 5.1). Bribie Island contains four ICOLLs, of which Welsby and Mermaid were investigated in this project (Figure 5.1). South Welsby is located
between these two ICOLLs and has similar characteristics to the two studied ICOLLs. However, South Welsby is classified as a coastal wetland as it does not open to the ocean, and was selected as a control site. The wetland (26.977° S; 153.156° E) is 150 m long, 15 m wide, has an average depth of 0.3 m and is about 150 m inland from the coastal sand dunes. Welsby ICOLL (26.965° S; 153.154° E) is about 0.7 km long, a maximum 40 meters wide and has an average depth of 0.4 m. Mermaid ICOLL (27.003° S; 153.167° E) is 1.3 km long, 70 m wide and has an average depth of about 0.4 m (Figure 5.1).

Bribie Island has a maximum elevation of less than 10 m with much of the island being either just above or below the water table, which has led to the creation of an extensive system of wetlands. The island is a sub-catchment of the Pumicestone regional catchment, covers an area of approximately 150 km², is around 30 km long and ranges from 5 to 7.5 km wide. Bribie Island has a subtropical climate with cooler, dry winters and warmer, wetter summers. Average annual rainfall on Bribie Island is 1420 mm with the majority (~60%) occurring over summer and spring periods. Over the course of this study, summer (Dec-Feb), autumn (Mar-May), winter (Jun-Aug) and spring (Sep-Nov) had seasonal rainfall of 191, 293, 201 and 160 mm, respectively (www.bom.gov.au). Urban development covers the southern end of the island with the remainder of the island consisting mainly of national park, proposed national park and state forest plantation. Pine plantation is currently being re-established in the centre of the island. National park covers 5580 ha, or approximately 40% of the island. Major vegetation types on the island are melaleuca open forest and wetland, and heath. The western side of the island supports extensive areas of intertidal mudflats, saltmarshes, mangroves and seagrasses (James and Bulley, 2004). The eastern edge of the island supports fire-sensitive beach ridge scrub and dune communities, and is also a Ramsar Wetland (Wetland of International Importance).

The groundwater resources of the island are divided into two water bodies. There is a regional surficial sand aquifer (shallow) which overlays a basal semi-confined aquifer (deep). The two aquifer units are separated by an indurated sand layer of varying thickness, porosity, and conformity throughout the Island. Water levels in the shallow aquifer follow the topography and groundwater occurs under unconfined conditions. For a full description of the Bribie Island aquifer system see Spring (2006). Groundwater in Bribie Island responds rapidly to rainfall as a result of the highly permeable sands (Armstrong, 2006). The high permeability of the sands and the low, flat topography restrict surface water runoff, with surface water only occurring as highly ephemeral streams, marshy swales and coastal
lagoons. The only significant surface water flow occurs after heavy rainfall periods (Spring, 2006). This study focussed on the eastern shoreline of Bribie Island. On the eastern coast, there is a narrow strip of foredunes. These dunes are approximately 10 m high and protect the coastal lagoons situated immediately behind them (Armstrong, 2006).

![Figure 5.1](image)

**Figure 5.1** Map of the study site. Red points indicate location of groundwater wells. The grey circle on Australia map indicates the study area.

### 5.2.2 Surface water surveys

Four sampling campaigns were performed in 2014 to enable seasonal comparison of groundwater discharge (5-7 February; 2-4 May; 12-14 August and 27-29 October). Automated radon monitors (RAD7, Durridge Co.) were used which averaged $^{222}\text{Rn}$ concentrations over 10 min intervals giving 2-σ uncertainties of 20–30% for each data point. The instrumentation was deployed on a small kayak and moved around the ICOLLS with a GPS marking the location of the readings. To measure $^{222}\text{Rn}$, a constant stream of surface water was pumped at approximately 3 L min$^{-1}$ into a gas equilibration exchanger (Dulaiova et al., 2005). The equilibrated air was then pumped in a closed-loop from the headspace of the
equilibrator chamber, through Drierite desiccant, and into the radon monitor. The partitioning of radon between the gas and the liquid phase was calculated as a function of temperature and salinity (Schubert et al., 2012). The radon activities are determined by counting the alpha-emitting, positively charged radioactive daughters ($^{218}$Po and/or $^{214}$Po), which are detected via a silicon detector (Schubert et al., 2006). Here, we measured $^{218}$Po only, as it has a secular equilibrium time of about 15 min. The $^{222}$Rn measurements were corrected assuming a time lag of 20 minutes (Stieglitz et al. 2010). This assumption is based on the time-lag of radon-in-air detectors relative to radon-in-water concentration, as the time required to detect a change in $^{222}$Rn activity in water varies from that in air, based on the pumping rate of water and the equilibration time in the RAD7 monitor of differing concentrations of $^{222}$Rn (Petermann and Schubert, 2015).

### 5.2.3 $^{222}$Rn diffusive and $^{226}$Ra decay experiments

For determining $^{222}$Rn diffusion from sediments, three sediment core samples were taken from each ICOLL and incubated in 60 cm long and 10 cm diameter cylinders. The cores were sealed and incubated with radium free water and left for a period of 1 month. This experiment was based on the assumption that after a month (i.e. > 5.5 half-lives for $^{222}$Rn), the only source of $^{222}$Rn (diffusion) will reach secular equilibrium with the only sink of $^{222}$Rn (decay) within the core (Santos and Eyre, 2011). Since diffusion driven radon concentrations will decrease with distance from the sediments (Várhegyi et al. 2013), the entire volume of water in the incubation cylinder was extracted into a six-liter gas tight bottle to prevent any concentration gradient effects. Thereafter, $^{222}$Rn concentration in the water column was measured using a RAD7 closed loop system from the bottom up preventing any effects of heterogeneity within the core. (Lee and Kim, 2006). Additionally, diffusion was independently calculated using a depth-independent approach following Equation (1) (Martens et al., 1980).

$$J_{\text{dif}} = (\lambda D_s)^{1/2} \left( C_{\text{eq}} - C_{\text{w}} \right)$$

(1)

where $\lambda$ is the $^{222}$Rn decay constant (0.181 day$^{-1}$); $D_s$ is the effective wet bulk sediment diffusion coefficient in sediment (m$^2$ d$^{-1}$). $C_{\text{eq}}$ is the average $^{222}$Rn concentration in groundwater (Bq m$^{-3}$) and $C_{\text{w}}$ is the average $^{222}$Rn concentration in the overlying surface water (Bq m$^{-3}$) (Corbett et al., 1998). We calculated $D_s$ as a function of temperature $D_s = \phi \cdot$
(10\(^{1.090/T}+1.59\)) (Ullman and Aller, 1982), while porosity (φ) was considered 0.4 based on sediment grain density (Armstrong, 2006).

To estimate the source of radon to the water column due to the decay of dissolved radium (\(^{226}\text{Ra}\)), approximately 40 L of water was collected from each ICOLL and passed through manganese impregnated fibre at 1 L min\(^{-1}\), which quantitatively absorbs the radium from the water (Moore and Arnold, 1996; Burnett et al., 2006). The filters were then rinsed with radium free water, partially dried and left for at least one month before being placed in a Radium Delayed Coincidence Counter (RaDeCC) for \(^{226}\text{Ra}\) concentration analysis (Peterson et al., 2009).

### 5.2.4 Groundwater sampling

Groundwater samples were collected seasonally from eight monitoring wells (all located in the upper aquifer) to characterize the composition of the groundwater seeping into the ICOLLs. The wells were installed by the Queensland Bulk Water Supply Authority (Seqwater) and located throughout the catchment (Figure 5.1). The wells ranged in depth from 4 to 19 m. In total 32 groundwater samples were collected. An inline pump was used to extract water from the wells and samples were taken after the wells were purged the equivalent of at least three times the well volume. A calibrated handheld multi-parameter probe (YSI) was used to determine salinity, pH, temperature, DO and conductivity for each sample. Gas tight six-liter plastic bottles were used to collect samples for radon analysis. These bottles are designed to prevent gas loss and \(^{222}\text{Rn}\) assessment can be immediately started in the field after sampling (Stringer and Burnett, 2004). Each six-liter bottle was connected to a RAD7 radon monitor and given at least two hours to achieve an air-water radon equilibrium with <5% uncertainty following well established protocols (Lee and Kim, 2006). The RAD7 was purged with dry fresh air for at least 30 min before running each sample to deplete all residual \(^{222}\text{Rn}\). Additionally, the sample water in each bottle was well mixed during measurements through RAD7 (Lee and Kim, 2006).

### 5.2.5 Radon mass balance

To estimate groundwater discharge into the lagoons, a \(^{222}\text{Rn}\) mass balance model described by Dimova et al. (2013) and Perkins et al. (2015) was applied. The model accounts for all known sources and sinks of \(^{222}\text{Rn}\) entering and leaving the system and assumes the missing \(^{222}\text{Rn}\) is due to groundwater discharge. The sources include \(^{222}\text{Rn}\) delivered by
groundwater discharge, $^{222}$Rn diffusion from sediments and $^{222}$Rn ingrowth from its parent isotope $^{226}$Ra while the sinks consist of radioactive decay and atmospheric loss of $^{222}$Rn. A conceptual model illustrating these sources and sinks is shown in Figure 5.2. The mass balance model applied for estimating groundwater discharge into lakes or lagoons assuming steady-state conditions is as below (Perkins et al., 2015):

$$(F_{gw} \cdot Rn_{gw}) + (D_{dif} \cdot A) + (^{226}Ra \cdot \lambda_{222} \cdot V) = (^{222}Rn \cdot \lambda_{222} \cdot V) + J_{atm} \quad (2)$$

where $F_{gw}$ is the groundwater discharge ($m^3$ $d^{-1}$); $Rn_{gw}$ is the groundwater endmember $^{222}$Rn concentration (Bq $m^{-3}$); $D_{dif}$ is $^{222}$Rn diffusive flux (Bq $m^{-2}$ $d^{-1}$); $A$ is the ICOLL surface area ($m^2$); $^{226}Ra \lambda_{222}V$ is radium decay (Bq $d^{-1}$) where $^{226}Ra$ is radium concentration in the water column, $\lambda_{222}$ is radon decay constant and $V$ is the volume of water in ICOLL; $^{222}Rn\lambda_{222}V$ is the radon decay (Bq $d^{-1}$) where $^{222}Rn$ is the $^{222}$Rn concentration in the water column and $J_{atm}$ is $^{222}$Rn atmospheric evasion (Bq $d^{-1}$). To calculate the groundwater flux for each ICOLL in each season the area weighted average surface radon concentration was used. This was used to prevent any bias resulting from small areas with high radon activity. This was done in ESRI ARCGIS 9.3 by using the average pixel value of the interpolated radon concentration map for each ICOLL in each season.

**Figure 5.2** Conceptual model of $^{222}$Rn mass balance approach used to quantify groundwater discharge into the ICOLLs. All relevant sinks and sources of $^{222}$Rn were quantified and the missing $^{222}$Rn was assigned to groundwater discharge.
Radon flux to the atmosphere depends on molecular diffusion generated by concentration gradients and turbulent transfer, which is dependent on physical processes (Macintyre et al., 1995). The evaluation of $^{222}$Rn loss to the atmosphere is based on an empirical equation that relates the gas–water exchange to solubility (as a function of temperature and salinity), wind velocity, and the air–water $^{222}$Rn gradient (Macintyre et al., 1995). The $^{222}$Rn atmospheric evasion flux ($J_{atm}$) was estimated as follows:

$$J_{atm} = k \left( C_w - \alpha C_{air} \right) A$$

where $C_w$ and $C_{air}$ are the $^{222}$Rn concentrations in water and air, respectively; $A$ is ICOLL area ($m^2$); $\alpha$ is the Ostwald solubility coefficient (dimensionless) describing the distribution of $^{222}$Rn at equilibrium as the fluid to-gas ratio; and $k$ is the piston velocity or the measure of the velocity of gas transfer at the air–water boundary ($m \, d^{-1}$). Piston velocity ($k$) driven by winds were estimated separately for each lagoon using (Wanninkhof 1992):

$$k_{wind} = 0.45u^{1.6} \left( Sc / 600 \right)^{-a}$$

where $u$ is wind speed ($m \, s^{-1}$); $Sc$ is the Schmidt number for $^{222}$Rn at a given water temperature; and $a$ is a variable power function dependent on wind speeds ($a = 0.6667$ for $u < 3.6 \, m \, s^{-1}$, and $a = 0.5$ when $u > 3.6 \, m \, s^{-1}$). The Schmidt number ($Sc$) was calculated based on formulations given by MacIntyre et al. (1995). Wind speed data were acquired from the Australian Bureau of Meteorology (www.bom.au) from the closest weather station (Beerburrum Forest Station) located 15 km away. The uncertainty of the $^{222}$Rn mass balance was calculated as a function of each individual term following the basic rules for error propagation. ICOLL areas were measured using satellite imagery imported from google earth and digitized in GIS. Depths were determined by taking the average of 10 random locations within each ICOLL.

5.3 Results

5.3.1 Environmental conditions

The region’s annual total rainfall for 2014 was 875.4 mm (www.bom.gov.au), which is about 40% lower than the average annual rainfall for Bribie Island (1420 mm y$^{-1}$). The dry
conditions throughout the year prevented any opening of the ICOLLs and therefore there was no visible water exchange between the ICOLLs and the ocean over the entire course of the study. Antecedent rainfall totals over the previous 10 years show dry conditions prevail in the winter and spring seasons (Table 5.1).

**Table 5.1** Rainfall in the region the month prior to sampling over a 10 year average, one month prior to sampling and one week prior to sampling.

<table>
<thead>
<tr>
<th>Season</th>
<th>10 year average one month prior (mm)</th>
<th>One month prior (mm)</th>
<th>One week prior (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer (5th February)</td>
<td>223</td>
<td>63</td>
<td>0.5</td>
</tr>
<tr>
<td>Autumn (2nd May)</td>
<td>160</td>
<td>110</td>
<td>31</td>
</tr>
<tr>
<td>Winter (12th August)</td>
<td>48</td>
<td>16</td>
<td>0</td>
</tr>
<tr>
<td>Spring (27th October)</td>
<td>88</td>
<td>13</td>
<td>7</td>
</tr>
</tbody>
</table>

**5.3.2 Welsby ICOLL**

Radon distribution varied spatially and temporally in Welsby ICOLL (Figure 5.3) with the highest concentrations observed in winter (up to ~ 54.5 Bq m⁻³) followed by autumn (up to 53.7 Bq m⁻³) (Table 2). During the summer, maximum ^222^Rn concentrations were 2.5 times lower than winter. The higher ^222^Rn concentrations (up to 54.5 Bq m⁻³ in winter) in the northern area of the ICOLL in all seasonal surveys indicated a possible hotspot for groundwater discharge. This may be due to higher topography to the north of the lagoon creating a steeper hydraulic gradient. The ^222^Rn concentrations were lower during summer indicating that higher rainfall directly over the ICOLL may cause dilution of the ICOLL water. There were hypersaline conditions (43.9 ppt) observed in summer, while Autumn had the lowest average salinity (23.4 ppt) (Table 2). The ICOLL remained closed during the monitoring period, which prevented any direct connection with the ocean. This led to hypersaline conditions despite higher rainfall in summer. This was likely due to higher summer temperatures, longer hours of sunlight and evaporation of the saline ICOLL waters following a previous inundation by seawater. There was spatial variation in salinity in the ICOLL, however there was similar distribution patterns in different seasons except for summer where higher peaks in salinity were seen (Figure 5.3). Both salinity and ^222^Rn concentrations were highest in the northern parts of the ICOLL during all seasons.
Chapter 5 | Intermittently Closed and Open Lakes and/or Lagoons (ICOLLs) as groundwater-dominated coastal systems: Evidence from seasonal radon observations

**Table 5.2** Maximum, minimum and average $^{222}\text{Rn}$ concentrations and salinity in Welsby, Mermaid ICOLLs and South Welsby lagoon during each survey time.

<table>
<thead>
<tr>
<th></th>
<th>Welsby</th>
<th>South Welsby</th>
<th>Mermaid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Summer</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radon (Bq m$^{-3}$)</td>
<td>0.3</td>
<td>22.5</td>
<td>10.3</td>
</tr>
<tr>
<td>Salinity</td>
<td>42.8</td>
<td>44.7</td>
<td>43.9</td>
</tr>
<tr>
<td><strong>Autumn</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radon (Bq m$^{-3}$)</td>
<td>4.5</td>
<td>53.7</td>
<td>27.2</td>
</tr>
<tr>
<td>Salinity</td>
<td>17.2</td>
<td>18.9</td>
<td>18.0</td>
</tr>
<tr>
<td><strong>Winter</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radon (Bq m$^{-3}$)</td>
<td>2.3</td>
<td>54.5</td>
<td>29.2</td>
</tr>
<tr>
<td>Salinity</td>
<td>11.7</td>
<td>27.4</td>
<td>19.5</td>
</tr>
<tr>
<td><strong>Spring</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radon (Bq m$^{-3}$)</td>
<td>1.3</td>
<td>43.2</td>
<td>24.5</td>
</tr>
<tr>
<td>Salinity</td>
<td>18.6</td>
<td>24.5</td>
<td>21.5</td>
</tr>
</tbody>
</table>

n.d. = no data.
Figure 5. 3 Contour maps of $^{222}\text{Rn}$ concentrations and salinity for Welsby ICOLL during seasonal field measurements. Note the different colour coding to highlight spatial trends in each season.
5.3.3 South Welsby Lagoon

South Welsby Lagoon was dry in the summer and could not be surveyed. Of the other seasons, the highest $^{222}\text{Rn}$ concentrations were observed in winter (up to $\sim 52.5 \text{ Bq m}^{-3}$), followed by spring and autumn (Table 2). Average $^{222}\text{Rn}$ concentrations in the lagoon did not vary considerably between seasons and ranged from $28.8\pm12.1 \text{ Bq m}^{-3}$ in autumn to $32.5\pm11.8 \text{ Bq m}^{-3}$ in winter (Table 2). The low salinities observed in the lagoon (ranging from 0.2 to 0.5 ppt) (Table 2) indicate the wetland has no connectivity with the ocean and cannot be classified as an ICOLL. The central parts (main body) of the wetland had elevated $^{222}\text{Rn}$ concentrations indicative of a groundwater discharge hotspot (Figure 5.4).
Figure 5.4 Contour maps of $^{222}$Rn concentrations and salinity for South Welsby Lagoon during seasonal field measurements. Dark parts indicate areas with no data due to very shallow water. Note the different colour coding to highlight spatial trends in each season.

### 5.3.4 Mermaid ICOLL

Similar to Welsby Lagoon, Mermaid ICOLL was closed during the entire duration of this study. This ICOLL had the lowest average surface water $^{222}$Rn concentrations (average yearly $^{222}$Rn concentration was 22.8±7.4, 30.6±10.5 and 13.7±4.0 Bq m$^{-3}$ ±SE for Welsby, South Welsby and Mermaid, respectively). In contrast to the other two systems where $^{222}$Rn was
highest in winter, Mermaid ICOLL had the highest $^{222}$Rn concentrations in spring (up to ~35.2 Bq m$^{-3}$) followed by autumn. This suggests the three systems do not necessarily follow the same seasonal groundwater discharge pattern, despite their close proximity. Salinity in Mermaid ICOLL had large temporal changes ranging from fresh in August (winter) to hypersaline in summer (Table 2), and had the highest average salinity among all the studied systems (34.5±2.4 ppt). The spatial distribution of $^{222}$Rn indicated that different areas of this ICOLL could potentially be groundwater discharge hotspots. The northern part of the ICOLL had relatively high $^{222}$Rn concentrations in every survey with higher topography in that area likely driving groundwater discharge. Additionally, high $^{222}$Rn concentrations in the small channels located in the middle parts of the ICOLL indicate groundwater seepage areas with groundwater likely entering the ICOLL from the west side and diluting as it moves towards the eastern side (Figure 5.5).
Figure 5.5 Contour maps of $^{222}\text{Rn}$ concentrations and salinity for Mermaid ICOLL during seasonal field measurements. Dark parts indicate areas with no data due to very shallow water. Note the different colour coding to highlight spatial trends in each season.
5.3.5 $^{222}$Rn diffusion

The estimated values using the depth independent approach were on average 0.7 Bq m$^{-2}$ day$^{-1}$, which is 60% lower than the average value estimated from sediment cores. As such we use the diffusion estimates from the core incubations throughout the mass balance, to provide a more conservative estimate of groundwater flow. Moreover, the peclet number defined as the advection to diffusion ratio was calculated to be 11.2 (average for two ICOLLS), indicting groundwater advection plays the major role in delivering groundwater to the ICOLLS, rather than diffusion.

5.3.6 Groundwater observations

Radon concentrations in groundwater samples ranged from 326 to 4019 Bq m$^{-3}$. The average groundwater $^{222}$Rn concentrations in all the seasons was 944 $\pm$ 171 (± SE) Bq m$^{-3}$ ($n$= 32) (Table 5.3). Average $^{222}$Rn concentrations varied in each season and were 1371±375, 377±75, 395±80 and 595±119 Bq m$^{-3}$ ± SE ($n$=8) in summer, autumn, winter and spring respectively. Average $^{222}$Rn concentrations in groundwater were 1–2 orders of magnitude higher than in the ICOLL surface waters (Table 4). Average $^{222}$Rn groundwater concentrations from samples collected in each season were used to obtain seasonal fluxes. All groundwater samples were fresh (salinities <0.5 ppt) and no correlations were observed between $^{222}$Rn and salinity in groundwater (not shown).
## Table 5.3 Groundwater observations.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Date</th>
<th>Closest system</th>
<th>Lat.</th>
<th>Long.</th>
<th>Depth (m)</th>
<th>Temp (°C)</th>
<th>Sal</th>
<th>pH</th>
<th>Cond. (mS cm⁻¹)</th>
<th>DO (mg L⁻¹)</th>
<th>**²²²Rn (Bq m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6/02/2014</td>
<td>Welsby</td>
<td>S26.965 E153.144</td>
<td>15.6</td>
<td>21.7</td>
<td>0.1</td>
<td>7.6</td>
<td>0.1</td>
<td>0.3</td>
<td>1344</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6/02/2014</td>
<td>Welsby</td>
<td>S26.965 E153.144</td>
<td>8</td>
<td>22</td>
<td>0.3</td>
<td>5.4</td>
<td>0.5</td>
<td>0.2</td>
<td>1765</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6/02/2014</td>
<td>South Welsby</td>
<td>S26.981 E153.149</td>
<td>16.5</td>
<td>22.9</td>
<td>0.1</td>
<td>5.1</td>
<td>0.3</td>
<td>0.1</td>
<td>881</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6/02/2014</td>
<td>South Welsby</td>
<td>S26.981 E153.149</td>
<td>6</td>
<td>24.6</td>
<td>0.1</td>
<td>4.8</td>
<td>0.3</td>
<td>0.1</td>
<td>4019</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>6/02/2014</td>
<td>Mermaid</td>
<td>S26.994 E153.156</td>
<td>18.8</td>
<td>26.4</td>
<td>0.1</td>
<td>5.6</td>
<td>0.2</td>
<td>0.2</td>
<td>698</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6/02/2014</td>
<td>Mermaid</td>
<td>S26.994 E153.156</td>
<td>12.8</td>
<td>24.9</td>
<td>0.1</td>
<td>4.9</td>
<td>0.2</td>
<td>0.2</td>
<td>884</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>6/02/2014</td>
<td>Mermaid</td>
<td>S26.994 E153.156</td>
<td>10</td>
<td>28.3</td>
<td>0.1</td>
<td>5.6</td>
<td>0.3</td>
<td>0.4</td>
<td>617</td>
<td></td>
</tr>
<tr>
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### Table 5.4 A summary of the terms used in the $^{222}$Rn mass balance model in the ICOLLs.

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<td>Summer</td>
<td>Autumn</td>
<td>Winter</td>
<td>Spring</td>
<td>Summer</td>
<td>Autumn</td>
<td>Winter</td>
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<td>27.0±7.8</td>
<td>29.3±8.1</td>
<td>24.5±6.7</td>
<td>n/d</td>
<td>28.8±9.6</td>
<td>32.5±8.9</td>
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<td>Ave. GW $^{222}$Rn (Bq m$^{-3}$)</td>
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<td>377.6±75.1</td>
<td>395.8±80.1</td>
<td>595.5±119.2</td>
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<td>377.6±75.1</td>
<td>395.8±80.1</td>
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<td>1919.4±384.0</td>
<td>377.6±75.1</td>
<td>395.8±80.1</td>
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<tr>
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<td>44,193</td>
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<td>700</td>
<td>725</td>
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<td>26,971</td>
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<td>Ave. wind speed at sampling time (m s$^{-1}$)</td>
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<td>6.1±1.2</td>
<td>6.1</td>
<td>7.6±1.5</td>
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<td>3.9±0.8</td>
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<td>Ave. daily wind speed (m s$^{-1}$)</td>
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<td>$^{222}$Rn evasion (Bq m$^{-2}$ d$^{-1}$)</td>
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<td>8.3±1.7</td>
<td>12.1±1.4</td>
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<td>0.3±0.1</td>
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<tr>
<td>$^{222}$Rn diffusion (Bq m$^{-2}$ d$^{-1}$)</td>
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5.4 Discussion

5.4.1 Quantifying groundwater discharge rates

The radon mass balance quantified the known $^{222}$Rn sources (i.e., diffusion from sediments and $^{226}$Ra decay) and sinks (i.e., decay and atmospheric evasion) (Table 4) with the missing term assigned to groundwater discharge. Considering the shallow depth (<0.5 m) of the ICOLLs, we assumed the water was vertically homogeneous. While higher temporal resolution data is needed to test the assumption of steady state conditions in ICOLLs, we assume the mass balance to be valid on a daily basis because the surface water level of the ICOLLs was seen to be stable during the period of sampling. Using wind speeds averaged over the previous 24 h, the radon mass balance revealed average groundwater discharge rates of 3.4±2.1, 7.3±8.9 and 2.6±1.7 cm d$^{-1}$ for Welsby, South Welsby and Mermaid, respectively (Table 5). The highest rate of groundwater discharge occurred during autumn into South Welsby Lagoon (12.5±10.6 cm d$^{-1}$) followed by Welsby ICOLL (5.1±3.0 cm d$^{-1}$) in winter. Overall, the model was highly sensitive to atmospheric losses, with evasion rates and associated uncertainties at least one order of magnitude higher than any other mass balance term (Table 4). Previous investigations of groundwater discharge into lakes have also found wind evasion to be the most important component in the radon mass balance (Cockenpot et al., 2015; Perkins et al., 2015; Dimova et al., 2013; Corbett et al., 2000).
Chapter 5 | Intermittently Closed and Open Lakes and/or Lagoons (ICOLLS) as groundwater-dominated coastal systems: Evidence from seasonal radon observations

Table 5.5 The groundwater discharge in Welsby and Mermaid ICOLL and South Welsby lagoon calculated from the $^{222}$Rn mass balance model.

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<tr>
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</tr>
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<td>4518±2461</td>
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<tr>
<td>GW discharge</td>
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<td></td>
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<td>10543±3064</td>
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<td>water volume per</td>
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<tr>
<td>day (%)</td>
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<tr>
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<td>water volume per</td>
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<tr>
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</tbody>
</table>
Previous studies using a radon mass balance to calculate groundwater discharge in lakes have used either average daily wind speed data or wind speed data at sampling time to estimate radon wind evasion. Wind speed data obtained during the time of surface water surveys was used by Dimova et al. (2013), while Kluge et al. (2012) used a long term (20 years) mean daily wind velocity to calculate evasion rates. Moreover, Gilfedder et al. (2015) suggested that by averaging wind speed measurements 5 to 10 days before sampling, more reasonable fluxes could be obtained. Here, we used the average daily wind speeds as sampling took place during the time of day when wind speeds were at their greatest. If we used wind speeds during sampling time with no localized wind attenuation at the surface of the ICOLLs, the model estimated groundwater discharge rates would increase by 147%, 63% and 165% for Welsby, South Welsby and Mermaid, respectively. In this scenario, average estimated groundwater discharge rates would be 8.4±3.0, 11.9±5.3 and 6.9±3.5 cm d$^{-1}$ for Welsby, South Welsby and Mermaid, respectively (Table 5). These values seem unrealistic considering the shallow nature of all ICOLLs. Wind attenuation due to vegetation surrounding wetlands may be very important (Gilfedder et al., 2015). Considering the ICOLLs are surrounded by vegetation, some wind attenuation was likely. If we assume a 50% wind attenuation, average groundwater discharge would be 1.6±1.8, 3.7±2.8 and 1.3±0.8 cm d$^{-1}$ for Welsby, South Welsby and Mermaid, respectively. We interpret these values as minimum groundwater discharge rates for the systems investigated. If an average daily wind speed data complied of 10 days before sampling was used to estimate wind evasion effect on radon concentration, evasion rates would not vary significantly except for autumn in South Welsby and Mermaid lagoons (Table 4) when compared to the average daily wind speed 24 h prior to sampling. Therefore, both approaches will result in very similar estimates (within 10%) of groundwater discharge rates. Regardless of any assumptions on wind speeds and associated $^{222}$Rn evasion, all these groundwater discharge rates are much higher than the potential surface water inputs into the ICOLLs (discussed later).

Dissolved $^{226}$Ra was measured once during the study period and applied to all seasons. The ICOLLs had highly variable salinities which could contribute to varying dissolved $^{226}$Ra activities (and therefore in-situ production rates for $^{222}$Rn) throughout the study period. If $^{226}$Ra concentrations were an order of magnitude higher during the non-sampled seasons, average annual groundwater discharge estimates would decrease by 3 to 27%. However, $^{222}$Rn produced through the decay of $^{226}$Ra was assumed to be negligible as the $^{226}$Ra decay
term has been reported previously to be a minor contributor (<5%) to the radon mass balance in coastal environments (Burnett and Dulaiova, 2003; Tait et al., 2013; Stewart et al., 2015).

Rainfall was highest during summer which corresponded with the lowest estimates of groundwater discharge. Lower rainfall during the winter coincided with higher groundwater inflow than the other seasons. Autumn had the highest groundwater discharge in South Welbsley and Mermaid ICOLLs (groundwater discharge in Welsby was fairly consistent). Summer had higher rainfall than autumn, but autumn had higher daily rainfalls than other seasons. This indicates that cumulative effect of smaller rainfall events during the month prior to survey may not efficiently recharge the groundwater system of the area as most of the rainfall happened in summer. Approximately 80% of rainfall on Bribie Island is reported to be lost through evapotranspiration before any recharge (Armstrong, 2006).

5.4.2 Groundwater role in ICOLLs hydrology

The estimated groundwater discharge rates indicate that groundwater contributed between 1% and 31% of the ICOLLs water volume in a day (i.e. groundwater discharge divided by ICOLL volume). There is limited surface water runoff into the ICOLLs on Bribie Island (Spring, 2006), and no surface flows were observed during the field investigations. A comparison between the average local annual precipitation (1420 mm y\(^{-1}\)) and the average annual groundwater discharge rates for each lagoon (12410, 26645, 9490 mm y\(^{-1}\)) revealed that groundwater input to the ICOLLs was equal to 89%, 94% and 87% of the total (rainfall + groundwater) annual water input, for Weslby, South Weslby and Mermaid, respectively. These estimates demonstrate that groundwater discharge plays a major role in the hydrology of Bribie Island ICOLLs. A decrease in groundwater levels may result in longer recharge times, leading to lower surface water levels that may potentially change the opening and closing regime of the ICOLLs. Although we did not observe surface runoff into the ICOLLs during sampling campaigns, it is likely that surface water inputs occur during heavy rain events when the sand becomes saturated (Armstrong, 2006). Additionally, some seepage is expected to occur from the ICOLL to the ocean due to the permeable berm and hydraulic gradient.

Since the ICOLLs were closed during our field investigations, we compare our observations to groundwater discharge estimates from a range of terrestrial and coastal lakes to put the results in perspective (Table 6). However, consideration must be given to the potential morphological differences between the study of ICOLLs and other lake systems due
to the high permeability of the sandy sediment underlying the ICOLLS. Past studies in lakes have shown that a low proportion (<1%) of lake water was replaced daily by groundwater discharge (Table 6). A recent review showed that median groundwater discharge rate into 107 lakes was 0.74 cm d\(^{-1}\) (Rosenberry et al., 2015). Our estimated average annual groundwater inflow is eight-fold higher than this average global rate. The higher proportion of groundwater discharge in ICOLLS may in part be due to the ratio of shoreline to lake volume. This ratio in previous studies of lakes was <0.006, however in this study the ratio was 0.046, 1.019 and 0.23 for Welsby, South Welsby and Mermaid Lagoon, respectively (Table 6; Figure 5.6). Higher shoreline to volume ratio may increase the relative contribution of groundwater discharge (Santos et al., 2012b). However, in most of these past studies, groundwater discharge exceeded direct rainfall input, demonstrating the importance of groundwater discharge in the hydrology of lakes.
Table 5. 6 Groundwater role in lake Hydrology from previous studies. Table updated from Perkins et al. (2015). ICOLLs are more groundwater-dominated than most other lakes.

<table>
<thead>
<tr>
<th>System name (location)</th>
<th>Ave. depth (m)</th>
<th>Ave. surface area (m²)</th>
<th>Volume (m³)</th>
<th>Shoreline length (m)</th>
<th>GW flux (cm d⁻¹)</th>
<th>Rainfall (cm d⁻¹)</th>
<th>Lake volume replaced in a day (%)</th>
<th>GW:Rain ratio over an annual cycle</th>
<th>Shoreline length: lake volume</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Welsby ICOLL (Australia)</td>
<td>0.4</td>
<td>88,386</td>
<td>36,459</td>
<td>1680</td>
<td>4.00</td>
<td>0.24</td>
<td>11.35</td>
<td>16.83</td>
<td>0.046</td>
<td>This study (2015)</td>
</tr>
<tr>
<td>South Welsby Lagoon (Australia)</td>
<td>0.3</td>
<td>3,137</td>
<td>785</td>
<td>800</td>
<td>5.40</td>
<td>0.24</td>
<td>14.9</td>
<td>16.74</td>
<td>1.019</td>
<td>This study (2015)</td>
</tr>
<tr>
<td>Mermaid ICOLL (Australia)</td>
<td>0.4</td>
<td>67,429</td>
<td>154,344</td>
<td>3560</td>
<td>3.40</td>
<td>0.24</td>
<td>6.50</td>
<td>14.33</td>
<td>0.023</td>
<td>This study (2015)</td>
</tr>
<tr>
<td>Sale Common Wetland (Australia)</td>
<td>2.0</td>
<td>3 × 10⁶</td>
<td>6 × 10⁶</td>
<td>10500</td>
<td>0.40</td>
<td>0.16</td>
<td>0.20</td>
<td>2.50</td>
<td>0.002</td>
<td>Geifedder et al., (2015)</td>
</tr>
<tr>
<td>Lake Ainsworth (Australia)</td>
<td>4.4</td>
<td>1.25 × 10⁵</td>
<td>550 × 10³</td>
<td>1690</td>
<td>0.67</td>
<td>0.49</td>
<td>0.37</td>
<td>1.37</td>
<td>0.003</td>
<td>Perkins et al., (2015)</td>
</tr>
<tr>
<td>Little lagoon (AL, USA)</td>
<td>1.5</td>
<td>10.5× 10⁶</td>
<td>1575× 10³</td>
<td>27555</td>
<td>1.45</td>
<td>0.45</td>
<td>0.01</td>
<td>3.22</td>
<td>0.002</td>
<td>Su et al., (2015)</td>
</tr>
<tr>
<td>Newmans lake (Florida, USA)</td>
<td>1.5</td>
<td>2.98 × 10⁷</td>
<td>44,700 × 10³</td>
<td>19500</td>
<td>0.50</td>
<td>0.36</td>
<td>0.002</td>
<td>1.39</td>
<td>0.000</td>
<td>Dimova et al., (2013)</td>
</tr>
<tr>
<td>Butler lake (Florida, USA)</td>
<td>4.2</td>
<td>6.38 × 10⁶</td>
<td>26,796 × 10³</td>
<td>17000</td>
<td>0.30</td>
<td>0.36</td>
<td>0.56</td>
<td>0.83</td>
<td>0.001</td>
<td>Dimova et al., (2013)</td>
</tr>
<tr>
<td>Clear lake (Florida, USA)</td>
<td>3.7</td>
<td>1.45 × 10⁶</td>
<td>5.365× 10³</td>
<td>4500</td>
<td>0.30</td>
<td>0.36</td>
<td>0.36</td>
<td>0.83</td>
<td>0.001</td>
<td>Dimova et al., (2013)</td>
</tr>
<tr>
<td>Haines lake (Florida, USA)</td>
<td>2.1</td>
<td>2.91 × 10⁶</td>
<td>6,111× 10³</td>
<td>7100</td>
<td>1.00</td>
<td>0.36</td>
<td>0.48</td>
<td>2.78</td>
<td>0.001</td>
<td>Dimova et al., (2013)</td>
</tr>
<tr>
<td>Shipp lake (Florida, USA)</td>
<td>1.5</td>
<td>1.12 × 10⁶</td>
<td>1.680× 10³</td>
<td>3770</td>
<td>0.10</td>
<td>0.36</td>
<td>0.07</td>
<td>0.28</td>
<td>0.002</td>
<td>Dimova et al., (2013)</td>
</tr>
<tr>
<td>Josephine lake (Florida, USA)</td>
<td>1.8</td>
<td>5.8 × 10⁶</td>
<td>10,440× 10³</td>
<td>14370</td>
<td>1.60</td>
<td>0.36</td>
<td>0.43</td>
<td>4.44</td>
<td>0.001</td>
<td>Dimova et al., (2013)</td>
</tr>
<tr>
<td>Marina lagoon (Egypt)</td>
<td>3.5</td>
<td>4× 10⁶</td>
<td>14× 10⁶</td>
<td>22000</td>
<td>6.00</td>
<td>0.13</td>
<td>0.02</td>
<td>46.2</td>
<td>0.002</td>
<td>El-Gamal et al. (2012)</td>
</tr>
<tr>
<td>Round lake (Florida, USA)</td>
<td>2.1</td>
<td>34,900</td>
<td>73,290</td>
<td>700</td>
<td>0.0</td>
<td>0.36</td>
<td>-</td>
<td>-</td>
<td>0.009</td>
<td>Dimova &amp; Burnett (2011)</td>
</tr>
<tr>
<td>SM8 (Canada)</td>
<td>0.9</td>
<td>1.91 × 10⁶</td>
<td>1,719× 10³</td>
<td>6700</td>
<td>0.05</td>
<td>0.12</td>
<td>0.56</td>
<td>0.42</td>
<td>0.004</td>
<td>Schmidt et al., (2010)</td>
</tr>
<tr>
<td>Lake Ammehshainer (Germany)</td>
<td>10.0</td>
<td>5.3 × 10⁵</td>
<td>5.6 × 10⁵</td>
<td>3265</td>
<td>18.6</td>
<td>0.16</td>
<td>17.61</td>
<td>116</td>
<td>0.006</td>
<td>Schmidt et al., (2009)</td>
</tr>
<tr>
<td>Mangleira (Brazil)</td>
<td>4.5</td>
<td>9 × 10⁸</td>
<td>4,050× 10⁶</td>
<td>216264</td>
<td>0.60</td>
<td>0.34</td>
<td>0.01</td>
<td>1.76</td>
<td>0.0001</td>
<td>Santos et al., (2008)</td>
</tr>
<tr>
<td>Willersinnweihre (Germany)</td>
<td>8.0</td>
<td>1.45 × 10⁵</td>
<td>1,160× 10³</td>
<td>2200</td>
<td>0.40</td>
<td>0.18</td>
<td>0.05</td>
<td>2.22</td>
<td>0.002</td>
<td>Kluge et al., (2007)</td>
</tr>
</tbody>
</table>
Figure 5.6 Shoreline length versus percentage of lake volume replaced in a day. Lake Ammelshainer in Schmidt et al. (2009) study has a very high lake volume replacement in a day and is considered an outlier.

There was a general negative relationship between surface lake area and the groundwater discharge to rainfall ratio over an annual cycle suggesting that even if groundwater discharge rates are small (because seepage is occurring over a large lake surface water area) they are a very important component to the lake water budgets. This highlights that groundwater is relatively more important than rainfall in the hydrology of ICOLLs (due to smaller surface area and shallow depth) and can have higher relative fluxes than other types of lakes. The high discharge in ICOLLs could also be due to the high hydraulic conductivity of the aquifer in this area. Previous studies have reported hydraulic conductivity values for Bribie Island ranging from 7 to 25 m d\(^{-1}\) (Harbison and Cox, 1998; Armstrong, 2006; Spring, 2006). The
well-sorted sands with high permeability and dunes overlying the regional aquifer are likely the main reason for this high conductivity. In other sandy coastal lagoons, a similar groundwater flux (6 cm d\(^{-1}\)) to that observed in this study (between 2.6 and 7.3 cm d\(^{-1}\)) has been reported (El-Gamal et al., 2012) (Table 6).

Calculated groundwater discharge rates are directly related to the radon concentration of the groundwater end-member meaning that higher radon concentrations in groundwater would result in lower groundwater discharge rates. Our radon end-member concentration was within the range of previous studies in regional shallow coastal aquifers along Australia’s east coast (Perkins et al., 2014; Makings et al., 2014; Gleeson et al., 2013, Maher et al., 2013, Atkins et al., 2013), but is lower than those reported in other coastal environments elsewhere (Dimova et al., 2013; Peterson et al., 2010).

Moreover, groundwater discharge for each ICOLL was calculated using the total area of each ICOLL. As the soil surrounding the ICOLLs is very permeable there is likely groundwater exchange across the barrier between the ICOLLs and the ocean which would be driven by differential pressure heads. This subsurface outflow means that the actual groundwater flux would be larger than the values reported since this subsurface groundwater loss term was not considered in the mass balance calculations. In future research, the installation of piezometers may help determine gaining and losing zones in the ICOLLs and provide information on the magnitude of head gradients and water losses through the permeable berm separating the ICOLLs from the ocean.

### 5.4.3 A tentative conceptual model

Our observations offer some conceptual insight into ICOLL hydrology as summarized in Figure 5.7. Radon may enter ICOLLs via fresh groundwater discharge driven by local hydraulic gradients and shallow porewater exchange driven by convection. ICOLLs often open during periods of high rainfall. Following the rainfall, seawater infiltrates the ICOLL at high tide. As this saline water in the ICOLLs is subject to evaporation in warmer, drier periods, with low fresh groundwater discharge, it becomes hypersaline. The difference in density between the overlying hypersaline waters and the brackish porewater can drive convective exchange at the sediment water interface and create salt fingers (Webster et al., 1996). This coupled with lower groundwater levels in drier periods would allow saline surface waters to permeate bottom sediments. While we have no salinity data in shallow ICOLL porewaters to test this hypothesis, previous studies have shown convection-driven
bottom water recirculation into estuaries sediments (Santos et al., 2012a; Robinson et al., 2007; Webster et al., 1996) and have mentioned the potential importance of this process (Rocha, 2000; Santos et al., 2012b; Maher et al., 2015).

Figure 5.7 A conceptual model describing groundwater discharge processes in ICOLLs. The upper panel demonstrates conventional salt fingers at the sediment-water interface when groundwater levels are low while the lower panel illustrates fresh groundwater discharge and saline groundwater forcing process when groundwater levels are higher.
With the discharge of $^{222}\text{Rn}$ enriched fresh groundwater into saline surface waters, a negative relationship between groundwater discharge and salinities was found (Figure 5.8) as has also been reported for other coastal lagoons (Su et al., 2014; El-Gamal et al., 2012). In both Welsby and Mermaid ICOLLs, groundwater discharge was lower in summer (high evaporation) while salinity was at its highest. These ICOLLs were closed to the ocean over the study period but have the highest salinity in the first sampling period (summer) indicating saltwater (ocean water) intrusion shortly before the commencement of the study. During wetter times, when groundwater levels rise, the shallow brackish to hypersaline porewater (now enriched in $^{222}\text{Rn}$) under the ICOLL may be forced back into surface waters creating localised $^{222}\text{Rn}$ hotspots with high salinity. To explain these instances of the localised coupling of high salinity and high radon concentrations, we present a conceptual model. As ICOLLs are shallow in nature (< 40 cm) and bottom sediments are made up of coarse sands, recirculation of the surface waters may be significant. This can occur through drivers such as density driven porewater exchange, bioirrigation and bioturbation (Santos et al., 2012) which cause surface water to infiltrate into the sediment, picking up a radon signal and discharging back into surface waters. However, the inverse relationship between salinity and groundwater discharge rates (Figure 5.8) implies a second scenario that fresh groundwater discharge (rather than saline porewater exchange) dominated $^{222}\text{Rn}$ sources during our investigations. Radon acts as a tracer for both fresh groundwater flux and recirculated groundwater flux.
Figure 5.8 Groundwater discharge versus salinity plots. South Welsby is not shown here as salinity did not vary in the wetland.

We are unable to quantitatively separate the relative contribution of fresh groundwater discharge versus saline porewater exchange driven by convection using $^{222}$Rn data only. Since fresh groundwater would be a source of new nutrients, and porewater would be a source of recycled nutrients (Weinstein et al., 2011), we suggest future studies use a combination of chemical tracers such as radium to resolve the contribution of these two water pathways to biogeochemical cycles in ICOLLs.

5.5 Conclusions

This study relied on the natural geochemical groundwater tracer $^{222}$Rn to quantify groundwater inflow into a coastal wetland and two ICOLLs. There was substantial spatial and temporal variability in $^{222}$Rn concentrations within the lagoons. The radon mass balance approach provided evidence that groundwater supplies a significant proportion of the recharge to Welsby, South Welsby and Mermaid Lagoons on Bribie Island with an average annual groundwater discharge rates of $3.4\pm2.1$, $7.3\pm8.9$ and $2.6\pm1.7$ cm d$^{-1}$ respectively. The estimated groundwater discharge rate in the ICOLLs was much larger than has been reported
in other lake systems probably because of the high permeability of surrounding soils and the high shoreline to lake volume ratio in ICOLLs. Over the study period, ~ 90% of water inputs to the ICOLLs were comprised of groundwater, demonstrating that the hydrology of Bribie Island ICOLLs is dominated by groundwater discharge.
Chapter 6

Greenhouse Gases and Submarine Groundwater Discharge in a Sydney Harbour Embayment (Australia)

Abstract

We investigated whether submarine groundwater discharge (SGD) traced by radon ($^{222}$Rn, a natural groundwater tracer) may drive carbon dioxide (CO$_2$), methane (CH$_4$) and nitrous oxide (N$_2$O) in surface waters in Chowder Bay, a marine embayment in Sydney Harbour, Australia. A radon mass balance revealed significant groundwater discharge rates into the bay (8.7 ± 5.8 cm d$^{-1}$). The average CO$_2$, CH$_4$, and N$_2$O concentrations in the subterranean estuary were 3.5, 7.2, and 2.8 times higher than the average surface water concentrations, indicating the possibility of coastal groundwater as a source of greenhouse gases to the bay. SGD-derived fluxes of greenhouse gases were 5.02 ± 2.28 mmol m$^{-2}$ d$^{-1}$, 5.63 ± 2.55 µmol m$^{-2}$ d$^{-1}$, and 1.72 ± 0.78 µmol m$^{-2}$ d$^{-1}$ for CO$_2$, CH$_4$ and N$_2$O, respectively. The average CO$_2$ evasion rate from surface water was 2.29 ± 0.46 mmol m$^{-2}$ d$^{-1}$ while CH$_4$ and N$_2$O evasion rates were 12.89 ± 3.05 and 1.23 ± 0.25 µmol m$^{-2}$ d$^{-1}$ respectively. Therefore, groundwater-derived greenhouse gas fluxes accounted for >100% CO$_2$ and N$_2$O and ~43% of CH$_4$ surface water evasion, indicating SGD is likely an important source of greenhouse gases to surface waters. However, this may be due to observations being performed near the SGD source, which may overestimate its contribution to the wider Sydney Harbour. On a 20-year time frame the combined emissions of CH$_4$ and N$_2$O from surface waters to the atmosphere accounted for 25% of the total CO$_2$-equivalent emissions. Although this study gives preliminary insight into SGD and greenhouse gas dynamics in Sydney Harbour, more spatial and temporal resolution sampling is required to fully constrain these processes.

**Key Words:** Radon, Subterranean Estuary, Greenhouse Gases, Carbon dioxide, Methane, Nitrous oxide, Chowder Bay.
Chapter 6 | Greenhouse Gases and Submarine Groundwater Discharge in a Sydney Harbour Embayment (Australia)

6.1 Introduction

Coastal ecosystems can play an important role in the global carbon cycling with most of the world estuaries being a source of the major greenhouse gases (i.e. carbon dioxide, methane and nitrous oxide) to the atmosphere (Borges and Abril, 2011; Bange et al., 1996). Disturbing natural coastal ecosystems and surrounding habitats may lead to significantly polluted waterways and the release of large amounts of buried carbon to the atmosphere (Lovelock et al., 2011; Adame et al., 2013). Previous studies have shown that SGD can deliver significant amounts of nutrients, dissolved carbon and trace metals to coastal waters (Beck et al., 2009; Knee et al., 2011; Porubsky et al., 2014; Lecher et al., 2015). More recently, several studies have suggested that submarine groundwater discharge (SGD) can also deliver large amounts of greenhouse gases such as CO$_2$, CH$_4$ and N$_2$O enriched groundwater into coastal surface waters (O’Reilly et al., 2015; Maher et al., 2015; Sadat-Noori et al., 2016). Solute concentrations, including contaminants, in groundwater are usually higher than in surface marine waters, making groundwater discharge a potentially important driver of surface water chemistry (Santos et al. 2009).

SGD is defined as any water derived by terrestrial and marine forces from the sediment into the surface water column (Moore et al., 2010). Common drivers of SGD are hydraulic head gradient, tidal pumping, and density-driven convection (Santos et al., 2012). Despite increased awareness, SGD remains poorly understood in several environments such as coastal megacities. For example, SGD studies on two major urbanized Asian megacities revealed that SGD derived dissolved inorganic nitrogen can account for up to 130 and 46% of the rivers nutrient input, demonstrating that SGD should be examined in more detail as an important source of biogeochemically active elements (Burrnet et al., 2007; Taniguchi et al., 2008).

Over the last two decades significant advances have been made with measurement techniques (natural geochemical tracers) to investigate SGD (Burrnet et al. 2006). Radon ($^{222}$Rn) is natural tracer which has proven to be effective tool in quantitatively investigating groundwater-surface water interactions. The main advantages of this tracer is its ability to integrate signals related to different groundwater pathways which may be useful in spatially heterogeneous and temporally dynamic systems (Stieglitz et al., 2010; Burnett et al., 2006). Additionally, $^{222}$Rn has conservative behaviour, occurs naturally in rocks and soil and has high concentration in groundwater in comparison to surface waters (Burnett et al. 2006). The short half-life of $^{222}$Rn (3.84 days) is advantageous as it is on the same scale as many physical
process related to groundwater discharge and physical mixing of coastal waters (Burnett et al., 2010).

The Sydney Harbour Estuary is the centrepiece of Australia’s largest city. This iconic waterway has immense social, economic and biological value (Smoothey et al., 2016). Sydney Harbour catchment accommodates approximately one-fifth of Australia’s population (4.8 million residents) (Banks et al., 2016), putting the catchment of the estuary under extensive industrial and coastal development pressure (Johnston et al., 2015; Birch et al., 2015). Although Sydney Harbour Estuary has been studied from the marine, biological and ecological perspectives in detail, the majority of these studies have focused on urban runoff (Stark, 1998), stormwater (Birch et al., 2010) and river inputs (Birch et al., 1996; Banks et al., 2016). Several studies on heavy metals within Sydney Harbour indicate benthic sediments are highly contaminated with heavy metals, but much lower concentrations are found in surface waters near the mouth of the estuary (Birch and Taylor 1999; Hatje et al., 2003; Birch et al., 2015). There are no previous studies addressing SGD and related chemical inputs into Sydney Harbour. Additionally, there is a lack of studies investigating hydrologic process within the Harbour and no time series data sets that identify trends and major drivers of biotic interactions (Johnston et al., 2015).

This study will, for the first time, quantify submarine groundwater discharge and its associated greenhouse gases (GHG) in an embayment from Sydney Harbour. Visible groundwater seeps around Sydney Harbour led us to hypothesize that SGD may be a major source of water and greenhouse gases to the Harbour. We test this hypothesis by conducting high frequency time series measurements of dissolved CO$_2$, CH$_4$ and N$_2$O in Chowder Bay, Sydney Harbour. We use a well-established groundwater tracer approach utilizing a $^{222}$Rn mass balance, to quantify groundwater advection rates and compare SGD-derived fluxes of greenhouse gas to fluxes at the surface water-air interface.

6.2 Material and methods

6.2.1 Site description

The study was conducted in Chowder Bay, a small cove in Sydney Harbour, Australia. Sydney Harbour is a heavily industrialized waterway surrounded by the city of Sydney (Figure 1). Sydney Harbour Estuary is ~30 km long, has an average depth of 13 m and is a very productive ecosystem containing a diverse variety of habitats and organisms. The
estuary’s upper and central sections are comprised of muddy sediment whereas the lower estuary has sandy bottom sediments (Birch et al., 2008). Estuary flushing times can vary from less than a day at the mouth of the estuary to up to 225 days in the upper parts (Das et al., 2006; Siboni et al., 2016). Chowder Bay is located close to the entrance of Sydney Harbour (33°50′48″S, 151°15′15″E), representing typical marine conditions with some potential influence of urban runoff and inputs from the upper estuary. Although the bay area is protected from dominant south easterly swells it is affected by wind-induced waves and storm swells (Hill et al., 2011). The seafloor is generally sandy with rocky reef outcappings and gentle slopes (Johnston et al., 2015).

**Figure 6.1** Map of the study site in Chowder Bay, Sydney, Australia.

Chowder Bay has an area of about 4300 m² and a catchment size of 0.5 km². The bay’s geological composition is sandstone with terrigenous sediments of fine grain size (Motta et
al., 2003). The habitat surrounding Chowder Bay is mainly soft sediments containing some seagrasses (*Zostera capricorni* and *Halophila ovalis*), shallow fringing rocky reefs and piers with wooden pilings (Glasby, 2001). The region receives ~1200 mm of rainfall annually and experiences a mild, warm, temperate climate all year round. Chowder Bay area is located at the low point within its sub-catchment and collects stormwater. The Parramatta River is the main tributary entering Sydney Harbour and has an annual mean water discharge flow of 1.5 m$^3$ s$^{-1}$ (Hatje et al., 2001). During dry weather conditions fresh-water discharge is low (<0.1 m$^3$ s$^{-1}$ at all discharge locations). Precipitation, freshwater inflow and evaporation are thought to mostly regulate salinity in Sydney Harbour (Lee et al., 2011). The harbour generally has the same salinity as the ocean (35) and is well mixed in dry periods. However, after rainfall the mouth of the Harbour can have salinity of about 30 in the upper 1-2 m (Hedge et al., 2014).

While a number of studies have addressed urban runoff (Stark, 1998), stormwater (Birch et al., 2010) and river inputs (Birch et al., 1996), this is the first investigation focusing on submarine groundwater discharge and greenhouse gases in Sydney Harbour. Moreover, there is a lack of studies investigating circulation and physical process within the harbour and no time series data sets that identify trends and major drivers of biotic interactions (Johnston et al., 2015). However, there is an extensive literature available on heavy metals within the harbour with the lowest concentrations at the mouth of the estuary near Chowder Bay (Birch and Taylor 1999; Hatje et al., 2003; Birch et al., 2015).

### 6.2.2 Surface water GHG and $^{222}$Rn time series

A field campaign was carried out from 19$^{th}$ to the 23$^{rd}$ November 2015. We deployed an automatic high frequency time series monitoring station on a jetty 80 meters from the shore within Chowder Bay (Figure 1). The station continually monitored water depth, salinity, temperature, dissolved oxygen, pH, $f$CO$_2$, $p$CH$_4$, N$_2$O and $^{222}$Rn over the duration of the field campaign. Surface water was pumped from 1 meter below the surface at a point where the average water depth was ~5 m. An automated $^{222}$Rn monitor (RAD7, Durridge Co.) averaged $^{222}$Rn concentrations over 30 minute cycles for about five days. Two cavity ring-down spectrometers (Picarro G2201-i- and G2308) coupled to a showerhead equilibrator were used to measure dissolved CO$_2$, CH$_4$ and N$_2$O at ~ 1 Hz (Maher et al, 2013) with data averaged over 1 minute intervals. Briefly, water was pumped at a constant rate of 3 L m$^{-1}$ to an equilibrator chamber where the gas in air and water reaches equilibrium. The equilibrated air
is then continuously pumped in a closed-loop from the headspace of the equilibrator chamber through desiccant (Drierite), the RAD7 and the Piccaros and then back to the equilibrator. The equilibration time for CO₂, CH₄, and ²²²Rn using this set up is ~ 5 min, 20 min, and 30 minutes respectively (Webb et al., 2016; Santos et al., 2012), with the equilibration time of N₂O assumed to be similar to CO₂ based on their similar solubilities (Arévalo-Martínez et al., 2013). CH₄ and N₂O fugacity were converted to concentrations based on the solubility coefficient calculated as a function of temperature and salinity (Wiesenburg and Guinasso, 1979; Weiss and Price, 1980). The sampling was conducted around neap tide with a tidal range from 0.8 m at the beginning of the campaign and increasing to 1.2 m towards the end (Figure 2). A calibrated Hydrolab (DX5) automatic logger was used to measure salinity (± 0.2), dissolved oxygen (± 0.2 mg L⁻¹) and water temperature (± 0.10 °C) at 15 min intervals while a depth logger (CTD diver) measured depth (± 0.01 m) at 10 min intervals. An Ocean pH Sensor (SAMI) was used to measure pH (± 0.003 units). Wind speed data (± 10%) were obtained from a weather station (Model PH1000) on site.
Figure 6. 2 Time series of surface water physico-chemical parameters, $^{222}\text{Rn}$ and greenhouse gases. Shaded areas indicate night time.
6.2.3 Groundwater sampling and analysis

A push point piezometer system was used to collect groundwater samples (Charette and Allen, 2006) across a salinity gradient from the high tide mark to the low tide mark. Shallow wells ranging between 0.5 – 2 m deep were dug on the beach near to the time series station (Figure 6.1) at low tide. A peristaltic pump was used to take samples after the wells were purged. The tubing was thoroughly flushed with the sample prior to sampling. A calibrated handheld YSI multiprobe was used to measure pH, temperature, DO and salinity for each groundwater sample. Samples for CO₂, CH₄ and N₂O were collected in gas-tight 250 ml bottles. Water was overflowed at least 3 times the bottle volume to which 200 µL of saturated HgCl₂ solution was added. Samples for groundwater ²²²Rn analysis were collected in six-litre gas-tight HDPE plastic bottles. Each bottle was connected to a RAD7 radon monitor and given at least 2 hours to achieve an air-water ²²²Rn equilibrium with <5% uncertainty following well established protocols (Lee and Kim, 2006). A total of 10 groundwater samples were collected.

Groundwater CO₂, CH₄ and N₂O samples were analyzed via a headspace method using a Picarro G2201-i-I and G2308 (Gatland et al., 2014). Briefly, 50 mL of sample water was drawn out using a gas syringe fitted with a hypodermic needle head while simultaneously 50 mL of synthetic CO₂, CH₄ and N₂O-free air was added to the sample. Bottles were then placed on a shaker for 1 min, placed upside down, and left for 18–24 h at room temperature to equilibrate. Thereafter, using a gas syringe, equilibrated air was extracted and 40 mL was expelled into gas tight 0.5 L Tedlar® film bags, while using 10 mL for flushing the lines beforehand. Samples were diluted with 350 mL of atmospheric air and before analysis on the Picarros.

6.2.4 ²²²Rn ingrowth and diffusion from sediments

To estimate ²²²Rn molecular diffusion from sediments, three sediment cores were sampled from the study area. Samples were incubated in 60 cm long and 10 cm in diameter cylinders. The cores were sealed and incubated with radium free water and left for a period of 1 month. This experiment was based on the assumption that after a month (>6 half-lives for ²²²Rn) the only source of ²²²Rn (diffusion) will reach equilibrium with the only sink (decay) within the core (Santos and Eyre, 2011). The overlying water in the incubation cores was extracted into six-liter gas tight plastic bottles and ²²²Rn concentration in the water was measured using a RAD7 and closed loop system (Lee and Kim, 2006). The entire water
column in each core was sampled from the bottom up preventing any effects of heterogeneity within the core. The diffusion fluxes were used in a $^{222}\text{Rn}$ mass balance to estimate SGD rates.

To assess the $^{222}\text{Rn}$ ingrowth from the decay of its parent isotope, $^{226}\text{Ra}$, two 80 L containers were filled with water, at low tide, and two 80 L samples were collected at high tide. The water was then passed through a magnesium fibre which quantitatively absorbs the radium from the water (Moore, 2003). The fibres were then sealed and left for at least 1 month before $^{226}\text{Ra}$ concentration analysis using a Radium Delayed Coincidence Counter (RaDeCC) (Peterson et al., 2009). These data were then used as an input to the $^{222}\text{Rn}$ mass balance.

### 6.2.5 SGD calculations and GHG fluxes

A non-steady state $^{222}\text{Rn}$ mass balance model was applied to estimate the groundwater discharge rate (cm d$^{-1}$) into the cove (Burnett and Dulaiova, 2003). Briefly, the model accounts for all sources (i.e. groundwater, diffusion from sediments, $^{226}\text{Ra}$ decay) and sinks (i.e. decay and atmospheric evasion) of $^{222}\text{Rn}$ entering and leaving the system. The model is based on the temporal (hourly) change of $^{222}\text{Rn}$ inventories in surface waters and accounts for $^{222}\text{Rn}$ ingrowth from dissolved $^{226}\text{Ra}$, $^{222}\text{Rn}$ decay (negligible at 1-hour time steps), atmospheric evasion losses and mixing with lower concentration offshore waters. In brief, $^{222}\text{Rn}$ concentration in the water column is corrected for $^{222}\text{Rn}$ not supported by $^{226}\text{Ra}$, then normalized to mean tidal height to remove the effect of changing inventories for each measurement interval (i.e. at flood tide corrections would be negative due to increase in depth and inventory). The tide normalized inventories are then corrected for atmospheric evasion losses for each measurement interval based on the equation described below. Additionally, mixing losses between Chowder Bay and the wider Harbour are estimated based on the rate of decrease of the radon inventory over each tidal cycle assuming the lowest concentrations observed during each mixing cycle (forced to match tidal cycles) represents the Harbour waters (Burnett and Dulaiova, 2003). The model has been widely applied to near-shore environments where no breaking waves are present such as Chowder Bay (e.g. Santos et al., 2009; Dulaiova and Burnett, 2006; Cyronak et al., 2014). Errors regarding the $^{222}\text{Rn}$ mass balance were calculated following the basic rules of error propagation.

Greenhouse gas fluxes derived from SGD (µmol m$^{-2}$ d$^{-1}$) were then calculated by multiplying the $^{222}\text{Rn}$-derived SGD rate by the average concentration of the gases in local
beach groundwater. Greenhouse gas atmospheric water to air fluxes were calculated using the equations of Wanninkhof (1992):

\[
F = k \alpha (C_{\text{water}} - C_{\text{air}})
\]

Where \( F \) is the flux of CO\(_2\), CH\(_4\) or N\(_2\)O in units of mmol m\(^{-2}\) d\(^{-1}\), \( C_{\text{water}} \) and \( C_{\text{air}} \) are the partial pressure of CO\(_2\), CH\(_4\) or N\(_2\)O in the water column and in air, respectively, in units of \( \mu \text{atm}; \) The atmospheric \( p_{\text{CO}_2}, p_{\text{CH}_4} \) and N\(_2\)O were assumed to be constant at an average of 400, 1.8 and 0.328 \( \mu \text{atm} \), respectively; \( \alpha \) is the solubility coefficient, calculated as a function of temperature and salinity using the constants of Weiss (1974) for CO\(_2\), Weiss, and Price (1980) for N\(_2\)O and Wiesenburg and Guinasso, (1979) for CH\(_4\); \( k \) is the gas transfer velocity at the water–air boundary (m d\(^{-1}\)). The main uncertainty associated with quantifying air-water gas exchange results from the estimation of gas transfer velocity, therefore \( k \) was calculated using the wind-speed based parameterization method of five different authors to provide a reasonable range in evasion rates (Wanninkhof, 1992; Crusius & Waninnkhof, 2003; Wanninkhof and McGillis, 1999; Raymond and Cole, 2001; and Borges et al., 2004). The transfer velocity equations rely on wind speeds \( (U) \) at a height of 10 m (m s\(^{-1}\)), the gas specific Schmidt number \( (Sc) \) at in situ temperatures and salinities (Wanninkhof 1992).

Water-to-air GHG fluxes were calculated using the average daily wind speeds collected on the site.

### 6.3 Results

#### 6.3.1 Surface water

During the field campaign there was no rainfall, however the area received a significant amount of rain (97 mm) in the 2 weeks prior to sampling. No surface runoff was present in Chowder Bay during field investigations even though surface runoff is known to occur following rain events. Average surface water temperature was 21.3 ± 0.1 °C while wind speeds were on average 2.8 ± 0.2 m s\(^{-1}\) leading to an average gas transfer velocity of ~ 1.8 ± 0.4 m d\(^{-1}\). Dissolved oxygen showed a diel cycle in the first half of the field campaign with higher values during the day and lower averages at night. However, this pattern was not apparent on the last two days of measurements (Figure 2). Salinity did not show a tidal trend.
and remained within a narrow range of 33.4 to 34.4 which illustrates the oceanic nature of the sampling location. pH showed typical oceanic values ranging from 8.05 to 8.20.

Concentrations of $^{222}$Rn had several peaks but were not clearly aligned with tides. $^{222}$Rn concentrations ranged from 5.6 to 15.9 Bq m$^{-3}$ and averaged 12.2 ± 2.1 Bq m$^{-3}$. Similarly, CO$_2$, CH$_4$ and N$_2$O did not follow a tidal trend and the daily variability decreased towards the end of the time series as tidal amplitudes increased. The three greenhouse gases were above atmospheric equilibrium (~ 400 µatm for CO$_2$, 2 nM for CH$_4$ and 7 nM for N$_2$O), indicating the cove was a source of CO$_2$, CH$_4$ and N$_2$O to the atmosphere. Partial pressure of CO$_2$ varied from 402 to 465 µatm with an average of 434 ± 2 µatm. CH$_4$ ranged from 5.7 to 12.6 nM with an average of 9.1 ± 0.3 nM while average N$_2$O was 8.1 ± 0.1 nM.

### 6.3.2 Groundwater

Salinity in groundwater samples ranged from fresh (0.3) to saline (34.8) with an average of 18.1 ± 4.1 (SE). The average $^{222}$Rn concentration was 358 ± 107 (SE) Bq m$^{-3}$, 29-fold higher than average surface water observations. The average CO$_2$, CH$_4$, and N$_2$O concentrations in groundwater were 3.5, 7.2, and 2.8 times higher than the average surface water concentrations (Table 6.1, Figure 6.3), indicating the possibility of groundwater as a source of greenhouse gases to the bay.

![Figure 6.3](image)

**Figure 6.3** The ratio of groundwater to surface water $^{222}$Rn and greenhouse gases ratios.
Table 6.1 Groundwater observations in Chowder bay, Sydney, Australia.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Date</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Salinity</th>
<th>pH</th>
<th>Temp (°C)</th>
<th>Depth below surface (m)</th>
<th>$^{222}$Rn (Bq m$^{-3}$)</th>
<th>CO$_2$ (µatm)</th>
<th>CH$_4$ (nM)</th>
<th>N$_2$O (nM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*GW 1</td>
<td>18/11/2015</td>
<td>33.83844</td>
<td>151.2543</td>
<td>0.3</td>
<td>6.89</td>
<td>25.1</td>
<td>3.5</td>
<td>340.9</td>
<td>12312.9</td>
<td>8056.9</td>
<td>17.0</td>
</tr>
<tr>
<td>GW 2</td>
<td>19/11/2015</td>
<td>33.83853</td>
<td>151.2542</td>
<td>0.5</td>
<td>9.24</td>
<td>23.5</td>
<td>3.0</td>
<td>177.6</td>
<td>1260.2</td>
<td>97.7</td>
<td>13.7</td>
</tr>
<tr>
<td>GW 3</td>
<td>18/11/2015</td>
<td>33.83865</td>
<td>151.2540</td>
<td>0.9</td>
<td>8.75</td>
<td>22.9</td>
<td>2.5</td>
<td>144.6</td>
<td>2028.7</td>
<td>79.3</td>
<td>13.4</td>
</tr>
<tr>
<td>GW 4</td>
<td>18/11/2015</td>
<td>33.83856</td>
<td>151.2544</td>
<td>17.5</td>
<td>7.81</td>
<td>21.7</td>
<td>2.0</td>
<td>119.2</td>
<td>1761.5</td>
<td>53.8</td>
<td>12.9</td>
</tr>
<tr>
<td>GW 5</td>
<td>18/11/2015</td>
<td>33.83858</td>
<td>151.2543</td>
<td>20.9</td>
<td>7.93</td>
<td>21.5</td>
<td>1.8</td>
<td>164.5</td>
<td>1893.3</td>
<td>87.4</td>
<td>15.5</td>
</tr>
<tr>
<td>GW 6</td>
<td>18/11/2015</td>
<td>33.83856</td>
<td>151.2544</td>
<td>34.8</td>
<td>7.75</td>
<td>21.0</td>
<td>1.0</td>
<td>181.9</td>
<td>2638.3</td>
<td>59.2</td>
<td>29.6</td>
</tr>
<tr>
<td>GW 7</td>
<td>19/11/2015</td>
<td>33.83858</td>
<td>151.2543</td>
<td>28.9</td>
<td>7.49</td>
<td>20.8</td>
<td>1.5</td>
<td>1018.5</td>
<td>1490.9</td>
<td>54.1</td>
<td>27.4</td>
</tr>
<tr>
<td>GW 8</td>
<td>19/11/2015</td>
<td>33.83861</td>
<td>151.2544</td>
<td>22.6</td>
<td>7.76</td>
<td>22.4</td>
<td>1.7</td>
<td>867.8</td>
<td>1226.3</td>
<td>55.9</td>
<td>23.4</td>
</tr>
<tr>
<td>GW 9</td>
<td>19/11/2015</td>
<td>33.8386</td>
<td>151.2543</td>
<td>26.6</td>
<td>7.92</td>
<td>22.6</td>
<td>1.0</td>
<td>39.4</td>
<td>2280.7</td>
<td>53.4</td>
<td>23.4</td>
</tr>
<tr>
<td>GW 10</td>
<td>19/11/2015</td>
<td>33.83855</td>
<td>151.2543</td>
<td>28.6</td>
<td>7.84</td>
<td>23.7</td>
<td>1.0</td>
<td>525.6</td>
<td>1009.9</td>
<td>41.2</td>
<td>20.9</td>
</tr>
</tbody>
</table>

Average 18.1 7.93 22.5 358.0 1732.2 64.7 19.7
Std dev 13.1 0.65 1.3 338.2 535.6 18.8 6.0
Std error 4.1 0.2 0.4 106.9 169.3 6.2 1.9

*Outlier excluded from CO$_2$ and CH$_4$ averages.
6.3.3 Flux estimates

The non-steady state $^{222}\text{Rn}$ mass balance model indicated that groundwater was discharging at an average rate of $8.7 \pm 5.8$ cm d$^{-1}$ (Figure 6.4). Estimated diffusive fluxes from the sediment core incubation experiment were $9.3$ Bq m$^{-2}$ d$^{-1}$ which was less than 15% of the advection rates from the mass balance, indicating groundwater advection has the major contributor of groundwater to the bay rather than diffusion. There were similar dissolved $^{226}\text{Ra}$ activities at low and high tide (average of $0.5 \pm 0.1$ Bq m$^{-3}$ (SE)). The production of $^{222}\text{Rn}$ through the decay of $^{226}\text{Ra}$ was negligible as average radium concentrations were <5% of $^{222}\text{Rn}$ activities in surface water. Previous studies have also reported $^{226}\text{Ra}$ decay and sediment diffusion to be a minor component of the $^{222}\text{Rn}$ mass balance in coastal areas influenced by SGD (Burnett and Dulaiova, 2006; Sadat-Noori et al., 2015; Tait et al., 2016).

![Figure 6.4](image.png)

**Figure 6.4** Groundwater advection rates over the study period. Error bars show propagated uncertainties.

Average atmospheric evasion losses were calculated at $10.1$ Bq m$^{-2}$ d$^{-1}$ while average losses from Chowder bay water mixing with the wider Harbour were estimate to be $38.2$ Bq m$^{-2}$ d$^{-1}$. The average piston velocity calculated by multiple methods available in the literature
was 1.8 ± 0.4 m d⁻¹ (Table 6.2). The highest piston velocity and consequently highest GHG evasion rates were estimated by formulation suggested by Borges et al., (2009) while the lowest piston velocity was estimated when the Wanninkhof & McGillis (1999) empirical equation was used. Average CO₂ evasion from surface water was calculated to be 2.29 ± 0.5 mmol m⁻² d⁻¹ while average CH₄ and N₂O evasion rates were 12.89 ± 3.05 and 1.23 ± 0.25 µmol m⁻² d⁻¹ (Table 6.2).

Using the calculated discharge rate, groundwater-derived CO₂ fluxes were estimated to be 5.02 ± 2.28 mmol m⁻² d⁻¹, while the groundwater-derived CH₄ and N₂O fluxes were 5.63 ± 2.55 and 1.72 ± 0.78 µmol m⁻² d⁻¹, respectively (Table 6.2, Table 6.3). These CO₂ and N₂O groundwater-derived fluxes were 2 and 1.5–fold larger than average surface water fluxes while groundwater CH₄ was about half of surface water fluxes.
Table 6.2 Greenhouse gas emission from surface water calculated using multiple piston velocity (k) methods available in the literature. Uncertainties indicate standard errors.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Average $K$ ($600/\text{CO}_2$) (m d$^{-1}$)</th>
<th>Average CO$_2$ Flux (mmol m$^{-2}$ d$^{-1}$)</th>
<th>Average CH$_4$ Flux ($\mu$mol m$^{-2}$ d$^{-1}$)</th>
<th>Average N$_2$O Flux ($\mu$mol m$^{-2}$ d$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k = 0.31U^2 (Sc/660)^{-1/2}$</td>
<td>1.4</td>
<td>1.79</td>
<td>9.90</td>
<td>0.93</td>
<td>Wanninkof (1992)</td>
</tr>
<tr>
<td>$k = 0.228U^{2.2} + 0.168$</td>
<td>1.5</td>
<td>1.94</td>
<td>10.74</td>
<td>1.01</td>
<td>Crusius &amp; Wanninkhof (2003)</td>
</tr>
<tr>
<td>$k = 0.0283U^3 (Sc/660)^{-1/2}$</td>
<td>0.8</td>
<td>1.07</td>
<td>5.82</td>
<td>0.53</td>
<td>Wanninkhof &amp; McGillis (1999)</td>
</tr>
<tr>
<td>$k = 1.91e^{0.35u} (Sc/660)^{-1/2}$</td>
<td>2.4</td>
<td>3.05</td>
<td>17.33</td>
<td>1.65</td>
<td>Raymond &amp; Coles (2001)</td>
</tr>
<tr>
<td>$k = 5.141u^{0.758} (Sc/660)^{-1/2}$</td>
<td>2.9</td>
<td>3.61</td>
<td>20.67</td>
<td>2.01</td>
<td>Borges et al. (2004)</td>
</tr>
<tr>
<td>Average</td>
<td>1.8±0.4</td>
<td>2.29±0.46</td>
<td>12.89±3.05</td>
<td>1.23±0.25</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.3 Groundwater advection rate and GW-derived GHG fluxes.

<table>
<thead>
<tr>
<th></th>
<th>Discharge rate</th>
<th>CO$_2$ (mmol m$^{-2}$ d$^{-1}$)</th>
<th>CH$_4$ (µmol m$^{-2}$ d$^{-1}$)</th>
<th>N$_2$O (µmol m$^{-2}$ d$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GW fluxes</td>
<td>8.7±5.8</td>
<td>5.02±2.28</td>
<td>5.63±2.55</td>
<td>1.72±0.78</td>
</tr>
<tr>
<td>Atmospheric evasion</td>
<td>2.29±0.46</td>
<td>12.89±3.05</td>
<td>1.23±0.25</td>
<td></td>
</tr>
</tbody>
</table>
6.4 Discussion

6.4.1 Submarine groundwater discharge

SGD rates based on the continuous $^{222}$Rn measurements in Chowder Bay showed semi-diurnal variability which suggests tidal pumping as a potential driver of SGD overlapping fresh SGD (Figure 4). The average groundwater advection rate ($8.7 \pm 5.8 \text{ cm d}^{-1}$) was indicative of considerable amount of groundwater discharging and interacting with bay surface water. Previous studies have reported a direct link and a significant inverse relationship between SGD and tidal height (Santos et al., 2011; Barnes et al., 2006; Bouillon et al., 2007; Call et al., 2015). Here, surface water $^{222}$Rn had no clear relationship with water levels (Figure 5) indicating that tidal pumping was not the only mechanism driving $^{222}$Rn dynamics. $^{222}$Rn concentrations in surface water peaked on low-low tides (day of 19/11 and night of 21/11 in Figure 2) and increased on high-low tide showing that tidal pumping may have occurred during larger tides. A potential additional driver of $^{222}$Rn was freshwater inputs from the upper Sydney Harbour, but this is unlikely because most of the upstream $^{222}$Rn would degas and decay by the time it reaches the outer Harbour area where we made our observations.

The wide range of salinities (0.3 - 34.8) observed in groundwater samples supports the notion of groundwater and surface water mixing in the subterranean estuary beneath the beach. This mixing within the subterranean estuary may explain the lack of correlation between $^{222}$Rn and salinity in groundwater samples (not shown) and suggests that combined marine (tidal pumping) and terrestrial (hydraulic gradient) forces drive SGD into the bay. Salinity often has little or no effect on radon concentrations in groundwater (Swarzenski, 2007; Burnett et al., 2007). Based on the morphology of the bay which is nestled between the harbour and steep hills, hydraulic gradient is assumed to also driver SGD. The wet conditions prior to measurements may have increased groundwater levels and related groundwater inputs. The $^{222}$Rn versus salinity scatter plot displayed a significant negative correlation (Figure 5). This implies that terrestrial freshwater inputs were dominant rather than recirculated seawater. The zero salinity intercept from $^{222}$Rn-salinity observations ($143 \pm 45 \text{ Bq m}^{-3}$) was about 50% of the average $^{222}$Rn concentration in beach groundwater ($285 \pm 87 \text{ Bq m}^{-3}$ excluding the high concentration outlier sample GW 7 in Table 1). Considering $^{222}$Rn losses in surface water via decay and atmospheric evasion, the intercept further suggests that
much of the $^{222}\text{Rn}$ was related to fresh rather than recirculated saline groundwater discharge to the bay.

The average $^{222}\text{Rn}$ concentration in groundwater samples was used as the endmember in the mass balance to calculate SGD. The error associated with using this average concentration (i.e. the standard error of all groundwater measurements) is propagated through the groundwater discharge calculations to highlight the uncertainty associated with this approach. Surface water runoff from storm water was not included in the mass balance because there was no visible surface flows into Chowder Bay over the course of the study. We suggest future studies use a combination of radioisotope tracers (radon and radium) along with comprehensive spatial and seasonal sampling to better identify water circulations patterns within Sydney Harbour and fully separate the contribution of fresh SGD and recirculated seawater to total SGD.

![Graph showing $^{222}\text{Rn}$ concentration versus depth and salinity.](image)

**Figure 6.5** Surface water $^{222}\text{Rn}$ concentration versus depth and salinity.

### 6.4.2 Greenhouse gas dynamics

A series of recent studies have shown a direct link between surface water $\text{fCO}_2$, $\text{CH}_4$, and $\text{N}_2\text{O}$ and groundwater exchange in coastal and estuarine systems (Wong et al., 2013; Santos et al., 2015; Call et al., 2015; Maher et al., 2015; O’Reilly et al., 2015). Here, a surface water $^{222}\text{Rn}$ versus $\text{fCO}_2$ scatter plot did not show a significant correlation (Figure 6.6), indicating groundwater may not be the primary driver of $\text{fCO}_2$ in the Bay. However, the positive correlation between $^{222}\text{Rn}$ concentrations in surface water and $\text{CH}_4$ and $\text{N}_2\text{O}$ implies that groundwater discharge may be driving these gases in surface waters (Figure 6.6). Any freshwater inputs from upstream were unlikely to be an important driver of $\text{fCO}_2$ in Chowder
Bay implied by the non-significant correlation between $\text{fCO}_2$ and salinity (Figure 6.7). Interestingly, both methane and nitrous oxide had stronger correlations with $^{222}\text{Rn}$ than with $\text{fCO}_2$. This may be related to CO$_2$ uptake by phytoplankton (Figure 6.8) driving $\text{fCO}_2$ concentrations on a diel cycle.
Figure 6.6 Surface water $^{222}\text{Rn}$ concentration versus greenhouse gas correlations.
Figure 6.7 Greenhouse gases in surface and groundwater versus salinity indicating fresh surface water is the primary source of GHG.
Salinity mixing plots imply that freshwater is a major source of CH$_4$ and N$_2$O to the bay surface waters (Figure 7). The positive correlation with $^{222}$Rn, in spite of large scatter, implies that SGD was a source of these gases. The $y$ intercept of the equation explaining CH$_4$ and N$_2$O versus $^{222}$Rn correlation implies that in the absence of $^{222}$Rn (i.e., SGD approaching zero) CH$_4$ would be 4.3 nM, which is higher than atmospheric equilibrium (2.1 nM) suggesting sources of CH$_4$ different than just SGD. However, the $y$ intercept would be 7.3 nM for N$_2$O which is close to the average surface water observations (8.1 ± 0.1) and similar to atmospheric equilibrium concentrations of 7.3 nM, suggesting groundwater as the main source of N$_2$O. There was no direct rainfall during the field campaign, therefore upstream river inputs and urban runoff are inferred as the main additional sources of CH$_4$ and N$_2$O. The Parramatta River had higher than base flow conditions at the time of sampling due to a total rainfall of 54.8 mm distributed over the week prior to sampling. High flow conditions are associated with high amounts of total nitrogen being delivered to the Harbour by river flow (Hedge et al., 2014) and may be responsible for higher concentrations of N$_2$O being delivered into the Harbour.
If we use the surface water CH$_4$ and N$_2$O zero salinity intercepts from the regression equations of the mixing plots (CH$_4$ = 205 nM at zero salinity; N$_2$O = 37.8 nM at zero salinity) and compare with the groundwater endmember we observed that surface water zero salinity intercepts were 3- and 2-fold higher, respectively, then the average beach groundwater concentrations. This indicates sources other than groundwater may drive the gases and/or some consumption of these gases occurs in the subterranean estuary. Estuarine surveys from the freshwater endmember to the mouth would help elucidate the role of upstream freshwater inputs of greenhouse gases to Sydney Harbour. When these zero salinity intercept concentrations are compared with river water endmember concentrations detected elsewhere, a close match is observed. A study on Brisbane River Estuary, Australia, with a water depth of 10 meters reported river CH$_4$ and N$_2$O concentrations to be 277 and 20 nM, respectively (Sturm et al., 2016), which were similar to the concentrations observed during this study. This supports the notion that a combination of SGD inputs and fresh surface water inputs from upstream may drive CH$_4$ and N$_2$O in Chowder Bay.

**6.4.3 SGD-derived GHG fluxes**

The water to air GHG fluxes showed that the bay was a source of CO$_2$ (2.29 mmol m$^{-2}$ d$^{-1}$), CH$_4$ (12.89 µmol m$^{-2}$ d$^{-1}$) and N$_2$O (1.23 µmol m$^{-2}$ d$^{-1}$) to the atmosphere (Table 2). Chowder Bay had CO$_2$ evasion rates much lower than the average fluxes observed in other lower estuaries with salinities higher than 25 (23.83 mmol m$^{-2}$ d$^{-1}$; Chen et al., 2013). For example, Maher et al. (2015) found average CO$_2$ fluxes of North Creek lower estuary, a subtropical tidal estuary located at NSW, Australia to be 10 mmol m$^{-2}$ d$^{-1}$. Call et al. (2016) reported an average CO$_2$ evasion rate of 9.4 mmol m$^{-2}$ d$^{-1}$ at the mouth of a tidal estuary located at Southern Moreton Bay, QLD, Australia. Here, primary productivity consuming CO$_2$ and mixing with near atmospheric equilibrium shelf waters are probably the main cause for the lower than average CO$_2$ fluxes. The influence of tidal dilution can also be seen in Figure 2, whereas when tidal amplitude increases towards the end of the time series, there is lower variability in $^{222}$Rn and GHG concentrations. This gradual increase of salinity could be a decrease in fresh groundwater discharge due to higher water levels (head) in the bay and/or a decrease in freshwater inputs to the wider Sydney Harbour.

Greenhouse gas concentrations in groundwater were much higher than those observed in the bay (Figure 3), resulting in a net greenhouse gas fluxes from groundwater to surface water and surface water to atmosphere (Table 3). The $^{222}$Rn mass balance provided quantitative results to build on the interpretation from the correlation analysis. The estimated fluxes of
groundwater-derived fluxes can account for 100% of the CO$_2$ and N$_2$O and 43% of the CH$_4$ surface water evasion fluxes, implying SGD was the major source of GHG to the Harbour. There was however a significant wind event during sampling which produced maximum wind speeds up to 8.1 m s$^{-1}$ leading to $k$ values as high as 7.5 m d$^{-1}$ which corresponded to a decrease in CH$_4$ and N$_2$O concentrations, but no obvious influence on $f$CO$_2$ or $^{222}$Rn concentrations.

The reported high contribution of SGD to GHG evasion is related to groundwater discharge being confined to a narrow seepage face near the location where measurements were conducted. While no information on the width of the seepage face is available for Chowder Bay, investigations elsewhere have shown seepage faces in the range of 1-200 m (Taniguchi et al., 2003; Paytan et al., 2006; Santos et al., 2009). Therefore, while SGD inputs of GHGs may only occur in this narrow seepage face close to our sampling station, evasion to the atmosphere can occur over a much larger area (Sydney Harbour is about 1500 m wide near Chowder Bay). This may create a false perception that groundwater is important in the entire Harbour. Since our estimates are localized and representative of a small embayment only, more spatial and temporal sampling is required to investigate this hypothesis in the wider Sydney Harbour. However, these flux estimates associated with the correlation analysis support our initial hypothesis that SGD is an important source of greenhouse gases in Sydney Harbour embayments.

6.4.4 CO$_2$-equivalent GHG emissions

Different greenhouse gases have different global warming potentials. In order to compare the overall contribution of the different greenhouse gases, CH$_4$ and N$_2$O were converted to CO$_2$-equivalent emissions from the bay assuming a 20 and 100 year sustained-flux global warming potential (Figure 9). Over a 20-year time frame, CH$_4$ and N$_2$O are 96 and 250 times more potent to impact global warming compared to CO$_2$ on a mass basis (Neubauer and Megonigal, 2015). Over a 100-year time frame, CH$_4$ and N$_2$O are 45 and 270 times more potent to impact global warming compared to CO$_2$ on a mass basis (Neubauer and Megonigal, 2015). On a 20-year time frame the combined emissions of CH$_4$ and N$_2$O accounted for 25% of the total CO$_2$-equivalent emissions in surface water while on a 100-year time frame this was 19% (Figure 9). For SGD-derived fluxes, CH$_4$ and N$_2$O accounted for about 10% of CO$_2$-equivalent emissions. Therefore, not accounting for SGD-derived CH$_4$ and N$_2$O emissions could overlook an important transport pathway of greenhouse gases into receiving waters. Our approach combining measurements of these three greenhouses gases
offers insights not only into their drivers, but may also help constraining local, regional and global greenhouse gas budgets.

![20 Year Time Frame](image)

![100 Year Time Frame](image)

**Figure 6.9** The contribution of the three major greenhouse gases in CO₂ equilivants using the 20- and 100-year Sustained-flux global warming potential of Neubauer and Megonigal (2015).

### 6.5 Conclusions

We presented the first $^{222}$Rn, carbon dioxide, methane and nitrous oxide surface water time series for a Sydney Harbour embayment (Chowder Bay). This is of importance for investigating the role of SGD on GHG emissions in urbanized aquatic environments. The results showed a significant amount of groundwater ($8.7 \pm 5.8 \text{ cm d}^{-1}$) was entering the bay as traced by $^{222}$Rn. Chowder Bay was a source of greenhouse gases to the atmosphere even
though water–air fluxes were smaller than similar systems. A radon mass balance suggested that SGD was a major source of greenhouse gases to the bay. Since our results are site specific, broader spatial and temporal coverage including the upper and middle parts of Sydney Harbour are required to better understand SGD rates and GHG dynamics in the Harbour.
7.1 Thesis conclusions

This thesis aimed to increase the knowledge on the role of submarine groundwater discharge on hydrology, carbon, nutrient and greenhouse gas dynamics in coastal aquatic systems. The main findings of this thesis are summarised as below:

1) A comprehensive spatial and temporal radon sampling strategy can produce groundwater discharge estimates with lower uncertainty and provide additional insights on where groundwater enters surface waters.

2) Groundwater dominated small estuarine systems have the ability to emit large amounts of CO$_2$ into the atmosphere from the water column and have large spatial and temporal variability in CO$_2$ emission (i.e. low in lower estuary and high in upper estuary). Additionally, groundwater discharge can be a significant source of greenhouse gases in large estuaries and the coastal ocean.

3) Groundwater discharge plays a significant role in coastal carbon dynamics and should be considered as an important component of the coastal carbon cycle.

4) Small estuarine systems can deliver more carbon and nutrients to the coastal waters compared to some larger riverine systems on a catchment area basis (carbon and nitrogen load dived by the catchments area).

5) The fresh and saline components of the discharging groundwater are significant sources of nutrients for coastal productivity and nutrient budgets and dynamics of coastal waters.

6) Groundwater discharge plays a significant role in the hydrology of ICOLLs.

To provide a synthesis of the conclusions from this thesis, the research questions posed in the introduction are discussed below:

1. **Would using multiple radon (222Rn) time series measurements decrease the overall groundwater discharge rate uncertainty?**

Chapter 1 showed that applying an extensive radon sampling strategy that covers spatial variabilities in a tidal estuary provides additional insights in the groundwater discharge area by breaking down the estuary into smaller sections. Additionally, this approach reduces the error resulting in lower uncertainty in the final groundwater discharge estimate. This chapter also highlighted that 222Rn and 224Ra can be used to complement each other as the groundwater discharge rate calculated from both tracers was shown to be in close agreement.
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Moreover, the combined use of these two natural geochemical tracer’s assists in separating the fresh and saline components of the discharging groundwater. For this case study area, the three endmember mixing model revealed that in wet conditions deep fresh groundwater is the dominant discharging groundwater with 65% contribution to the overall groundwater discharge while during dry conditions shallow saline groundwater (or recirculated estuary water) contributes a larger portion (80%).

2. **Is SGD a significant source of carbon and greenhouse gases in subtropical estuaries and an important component of the global carbon cycle?**

In chapter 3, the groundwater discharge rate estimated in chapter 2 using the multiple time series strategy was used to calculate groundwater-derived carbon inputs to the estuary surface water. This chapter highlighted that groundwater-derived carbon inputs were a significant component of the carbon export from the estuary to the coastal ocean regardless of the amount of rainfall in the proceeding months. Additionally, groundwater discharge accounted for about 50% of the estuary-wide CO$_2$ and CH$_4$ evasion rates again indicating the significant role of groundwater in carbon dynamics in coastal estuaries. Assuming similar conditions to this case study for other estuaries in subtropical areas around the world, groundwater discharge in coastal environments has the potential to significantly influence the global carbon cycling.

Additionally, chapter 3 highlights that the Hat Head small estuary (25 m width and 5 km length) had the capacity to export several fold higher DIC and DOC relative to its catchments size than the global average estuarine carbon export. This is likely due to the short residence of the estuary which reduces the time for biogeochemical reactions. Moreover, on a unit per catchment area basis, the Hat Head estuary had the ability to export a large amount of dissolved carbon compared to larger riverine system with higher surface water discharge. This chapter also highlighted the spatial heterogeneity and temporal variability of surface water CO$_2$ evasion within a small size estuary. The results presented in this chapter suggest that groundwater derived carbon is a major component of the coastal carbon cycle.

3. **Is fresh and recirculated SGD a major pathway for nutrient delivery to small subtropical estuaries?**

Chapter 4 outlined the relative contribution of deep fresh and shallow saline groundwater nutrient inputs during wet and dry seasons. Deep fresh groundwater dominated nutrient inputs in the wet season and shallow saline groundwater delivered more nutrients in the dry
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season. The chapter shows that groundwater discharge can deliver large amount of both inorganic and organic nutrients to estuarine waters regardless of the source. This supply of nutrients to the estuary can change surface water N:P ratios from typical N-limiting conditions to P-limiting. This was especially noticeable during low tide in the wet season when groundwater discharge into the estuary was higher. This chapter also highlighted that groundwater discharge can be a significant player in potential changes in phytoplankton community in estuarine environments and the nearby coastal ocean since the composition of coastal phytoplankton community is usually regulated by DIN availability. Therefore, it is suggested that strategies to manage eutrophication on coastal waters scale should address both groundwater and surface water sources.

Chapter 4 also illustrates that not only small estuaries can act as a source of nutrients to the coastal waters but they can deliver more nutrients compared to larger riverine systems. For example, the small Hat Head estuary exported 7-times more DIN and 2-times more DIP than the global average riverine DIN and DIP export, respectively. This was likely due to the surrounding wetlands and nutrient-enriched groundwater inputs in this region. This indicates that although estuaries cover a small percentage of the world-wide surface area they should be considered an important component of the global nutrient budgets.

4. What is the role of groundwater discharge on the hydrology of intermittently closed and open coastal lakes or lagoons?

Chapter 5 demonstrated that the hydrology of ICOLLs is dominated by groundwater discharge rather than direct precipitation even though observations were made in a dry year with presumably lower-than-average groundwater discharge rates. It was found that over the study period, ~ 90% of water inputs to the ICOLLs were comprised of groundwater. Therefore, groundwater level fluctuations in Bribie Island have the potential to affect the hydrology of these ICOLLs. Moreover, this chapter demonstrates that $^{222}$Rn is an effective tool for quantifying groundwater discharge in remote and unmonitored coastal systems areas where no hydrogeological data such as groundwater level, hydraulic gradient and aquifer thickness, is available.

5. Is SGD a major source of greenhouse gases in large scale estuaries such as bays?

Chapter 6 highlights the role of groundwater discharge in greenhouse gas dynamics in larger estuarine systems such as Sydney Harbour estuary. The chapter presented the first CO$_2$, CH$_4$ and N$_2$O data for this urbanized estuary and the results show that fresh
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groundwater seeps into the coastal waters of this estuary and that SGD can be a major source of greenhouse gases to the embayment. This chapter also highlighted the significant role of groundwater discharge in greenhouse gas evasion from the estuary surface water to the atmosphere.

In summary, the thesis documents the use of complex mass balance modelling combined with a multi-tracer approach, to quantify, interpret and manage groundwater discharge in coastal systems. The dynamic characteristics of groundwater discharge may require large, intensive and multi-faceted sampling strategies to effectively quantify and constrain its effects on coastal surface water quality. Dissolved carbon, greenhouse gases and nutrient export from small estuaries are strongly coupled to groundwater discharge therefore should not be neglected in coastal carbon and nutrient budget studies. This thesis highlights that groundwater-derived constituent fluxes from small subtropical estuaries into the coastal ocean can rival those delivered from rivers. Additionally, this dissertation looks closely into the drivers of fresh and saline SGD and illustrates that the fresh and saline components of the discharging groundwater have different contributions in delivering dissolved constituents to coastal estuaries. Moreover, results presented here support the notion that even small volumetric groundwater fluxes occurring on large scales have a major role in the hydrology and biogeochemistry of coastal ecosystems.

7.2 Recommendations and future work

Although this thesis makes an attempt to decrease the current uncertainties related to SGD estimations, there still remains a number of issues in this field that require further investigation. Therefore, I would like to make the following recommendations for future studies on understanding SGD processes and estimating its associated chemical fluxes:

- Firstly, an enormously important aspect of understanding SGD and its associated dissolved chemical fluxes, lies within the fundamental processes that lead to the solute flux. For instance, a better understanding of the groundwater endmember composition, which is often considered variable and heterogeneous, is clearly needed. This term plays a significantly important role in the mass balance model and ultimately in quantifying and estimating solute fluxes associated with SGD. I recommend future studies investigate how heterogeneous groundwater endmembers
maybe and what causes such variations in groundwater endmembers. The understanding of these processes can lead to a flux estimate on a global scale with low uncertainties.

- Secondly, utilizing geochemical tracers to quantify nutrient delivery to coastal surface waters is an internationally recognised and accepted approach. However, nutrients such as nitrogen and phosphorous are highly reactive and their concentrations can alter along the submarine groundwater discharge flow path. Hence, values calculated using this method may not represent an accurate flux of these solutes to surface waters. Therefore, to reduce uncertainties related with this method, future work should focus on processes that could affect the concentration and speciation of nutrients as the water flows from the groundwater sampling point to the discharge point where it enters surface waters.

- SGD has been shown to play an important role in greenhouse gas cycling. From the three primary greenhouse gases, estimates of SGD-derived N₂O fluxes are extremely important because they are rarely studied and N₂O is the most potent of the three major greenhouse gases. Furthermore, reactive nitrogen in earth surface processes is increasing rapidly as humans fix unreactive atmospheric N₂ to reactive forms such as ammonium and nitrate. The N₂O fluxes associated with SGD would therefore be expected to continue to increase into the future, making this avenue of research important. Therefore, future studies should focus on such processes as this understanding will be required for any potential mitigation of this greenhouse gas source.
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Groundwater discharge into an estuary using spatially distributed radon time series and radium isotopes

Mahmood Sadat-Noori a,b,*, Isaac R. Santos a,b, Christian J. Sanders a,b, Luciana M. Sanders c, Damien T. Maher a

a School of Environment, Science and Engineering, Southern Cross University, Lismore, New South Wales, Australia
b National Marine Science Centre, School of Environment, Science and Engineering, Southern Cross University, Coffs Harbour, New South Wales, Australia
c Southern Cross GeoScience, Southern Cross University, Lismore, New South Wales, Australia

SUMMARY

Quantifying groundwater discharge remains a challenge due to its large temporal and spatial variability. Here, we quantify groundwater discharge into a small estuary using radon (222Rn) and radium isotopes (223Ra and 224Ra). High temporal resolution (30 min time steps) radon observations at 4 time series stations were used to determine where groundwater discharge is prevalent in the estuary, and to reduce mass balance model uncertainties. A three-endmember mixing model was developed based on short-lived radium isotopes (sampled at a single location) to separate the shallow saline and deep fresh sources of the discharging groundwater. The results show that using multiple 222Rn time series stations decreased the overall uncertainty of groundwater discharge estimates from about 41% to 23%. The radon derived groundwater flux was 56 ± 13 and 35 ± 12 cm d⁻¹ in wet and dry conditions, respectively. The spatially distributed stations detected a well-defined small area located four kilometers upstream from the mouth of the estuary as a groundwater discharging hotspot. Estimates based on a 223Ra and 224Ra mass balance resulted in groundwater discharge estimates of 65 ± 18 and 84 ± 48 cm d⁻¹ in the wet and 18 ± 5 and 20 ± 6 cm d⁻¹ in the dry. The mixing model revealed contrasting results for deep vs. fresh groundwater contribution in wet and dry conditions. In wet conditions, deep fresh groundwater discharging into the estuary contributed 65% compared to the shallow saline groundwater (35%), while during dry conditions a larger contribution (80%) was related to shallow groundwater. A comprehensive spatial and temporal sampling strategy can produce groundwater discharge estimates with lower uncertainty and provides additional insight on where groundwater enters surface waters.

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Groundwater Discharge as a Source of Dissolved Carbon and Greenhouse Gases in a Subtropical Estuary

Mahmood Sadat-Noori¹,² · Damien T. Maher¹ · Isaac R. Santos¹,²

Abstract Groundwater may be highly enriched in dissolved carbon species, but its role as a source of carbon to coastal waters is still poorly constrained. Exports of deep and shallow groundwater-derived dissolved carbon species from a small subtropical estuary (Korogoro Creek, Australia, latitude −31.0478°, longitude 153.0649°) were quantified using a radium isotope mass balance model ([²³³Ra and [²²⁴Ra, natural groundwater tracers) under two hydrological conditions. In addition, air-water exchange of carbon dioxide and methane in the estuary was estimated. The highest carbon inputs to the estuary were from deep fresh groundwater in the wet season. Most of the dissolved carbon delivered by groundwater and exported from the estuary to the coastal ocean was in the form of dissolved inorganic carbon (DIC; 687 mmol m⁻² estuary day⁻¹; 20 mmol m⁻² catchment day⁻¹, respectively), with a large export of alkalinity (23 mmol m⁻² catchment day⁻¹). Average water to air flux of CO₂ (869 mmol m⁻² day⁻¹) and CH₄ (26 mmol m⁻² day⁻¹) were 5- and 43-fold higher, respectively, than the average global evasion in estuaries due to the large input of CO₂- and CH₄-enriched groundwater. The groundwater discharge contribution to carbon exports from the estuary for DIC, dissolved organic carbon (DOC), alkalinity, CO₂, and CH₄ was 22, 41, 3, 75, and 100 %, respectively. The results show that CO₂ and CH₄ evasion rates from small subtropical estuaries surrounded by wetlands can be extremely high and that groundwater discharge had a major role in carbon export and evasion from the estuary and therefore should be accounted for in coastal carbon budgets.

Keywords Submarine groundwater discharge · Surface water–groundwater interaction · Carbon dioxide · Methane · Permeable sediments · Radon · Cavity ring down spectrometry · Mangrove · Greenhouse gases

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Mahmood Sadat-Noori
m.sadatnoori@yahoo.com

1 School of Environment, Science and Engineering, Southern Cross University, PO Box 157, Lismore NSW 2480, Australia

2 National Marine Science Centre, Southern Cross University, PO Box 4321, Coffs Harbour NSW 2450, Australia
Intermittently Closed and Open Lakes and/or Lagoons (ICOLLs) as groundwater-dominated coastal systems: Evidence from seasonal radon observations

Mahmood Sadat-Nooria,b,⇑, Isaac R. Santosa,b, Douglas R. Taita,b, Ashly McMahonab, Sean Kadelc, Damien T. Maherb

aNational Marine Science Centre, Southern Cross University, Coffs Harbour, New South Wales, Australia
bSchool of Environment, Science and Engineering, Southern Cross University, Lismore, New South Wales, Australia
cQueensland Bulk Water Supply Authority (Seqwater), Queensland, Australia

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SUMMARY

Intermittently Closed and Open Lakes or Lagoons (ICOLLs) are dynamic coastal systems that may be vulnerable to changes in catchment hydrology. However, little is known regarding the role of groundwater on the hydrological cycles of ICOLLs. Groundwater discharge in two ICOLLs (Welsby and Mermaid) and a nearby wetland (South Welsby Lagoon) located on Bribie Island (Australia) was quantified using radon (222Rn, a natural geochemical groundwater tracer) during four seasonal surveys. The distribution of radon revealed temporal and spatial changes over the study period with higher surface water radon concentrations found in winter for Welsby ICOLL and in autumn for Mermaid ICOLL. The average estimated groundwater discharge rates from a radon mass balance were 3.4 ± 2.1, 7.3 ± 8.9 and 2.6 ± 1.1 cm d⁻¹ in Welsby, South Welsby and Mermaid Lagoons, respectively. These values are at least 8-fold greater than the average annual precipitation that falls directly over the ICOLLs (1420 mm per year, or 0.4 cm d⁻¹), which, coupled with minimal surface water runoff due to the permeable sandy soils, demonstrates that these systems are groundwater-dominated. Overall, groundwater discharge rates in these ICOLLs were much larger than has been reported in other lake systems which is most likely due to the high permeability of regional sandy soils and their large shoreline to volume ratio.

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Fresh meteoric versus recirculated saline groundwater nutrient inputs into a subtropical estuary

Mahmood Sadat-Noori a,b,⁎, Isaac R. Santos a, Douglas R. Tait a,b, Damien T. Maher b

a National Marine Science Centre, School of Environment, Science and Engineering, Southern Cross University, Coffs Harbour, NSW, Australia
b School of Environment, Science and Engineering, Southern Cross University, Lismore, NSW, Australia

Abstract

The role of groundwater in transporting nutrients to coastal aquatic systems has recently received considerable attention. However, the relative importance of fresh versus saline groundwater-derived nutrient inputs to estuaries and how these groundwater pathways may alter surface water N:P ratios remains poorly constrained. We performed detailed time series measurements of nutrients in a tidal estuary (Hat Head, NSW, Australia) and used radium to quantify the contribution of fresh and saline groundwater to total surface water estuarine exports under contrasting hydrological conditions (wet and dry season). Tidally integrated nutrient fluxes showed that the estuary was a source of nutrients to the coastal waters. Dissolved inorganic nitrogen (DIN) export was 7-fold higher than the average global areal flux rate for rivers likely due to the small catchment size, surrounding wetlands and high groundwater inputs. Fresh groundwater discharge was dominant in the wet season accounting for up to 45% of total dissolved nitrogen (TDN) and 48% of total dissolved phosphorus (TDP) estuarine exports. In the dry season, fresh and saline groundwater accounted for 21 and 33% of TDN export, respectively. The combined fresh and saline groundwater fluxes of NO₃, PΟ₄, NH₄, DON, DOP, TDN and TDP were estimated to account for 66, 58, 55, 31, 21, 53 and 47% of surface water exports, respectively. Groundwater-derived nitrogen inputs to the estuary were responsible for a change in the surface water N:P ratio from typical N-limiting conditions to P-limiting as predicted by previous studies. This shows the importance of both fresh and saline groundwater as a source of nutrients for coastal productivity and nutrient budgets of coastal waters.

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⁎ Corresponding author at: School of Environment, Science and Engineering, Southern Cross University, PO Box 157, Lismore, NSW 2480, Australia.
E-mail address: mahmood.sadat-noori@scu.edu.au (M. Sadat-Noori).
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Greenhouse gases and submarine groundwater discharge in a Sydney Harbour embayment (Australia)

Mahmood Sadat-Noori a, b, *, Douglas R. Tait a, b, Damien T. Maher b, Ceylena Holloway a, b, Isaac R. Santos a, b

a National Marine Science Centre, School of Environment, Science and Engineering, Southern Cross University, Coffs Harbour, NSW, Australia
b School of Environment, Science and Engineering, Southern Cross University, Lismore, NSW, Australia

ABSTRACT

We investigated whether submarine groundwater discharge (SGD) traced by radon (222Rn, a natural groundwater tracer) may drive carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) in surface waters in Chowder Bay, a marine embayment in Sydney Harbour, Australia. A radon mass balance revealed significant groundwater discharge rates into the bay (8.7 ± 5.8 cm d⁻¹). The average CO₂, CH₄, and N₂O concentrations in the subterranean estuary were 3.5, 7.2, and 2.8 times higher than the average surface water concentrations, indicating the possibility of coastal groundwater as a source of greenhouse gases to the bay. SGD-derived fluxes of greenhouse gases were 5.02 ± 2.28 mmol m⁻² d⁻¹, 5.63 ± 2.55 mmol m⁻² d⁻¹, and 1.72 ± 0.78 mmol m⁻² d⁻¹ for CO₂, CH₄ and N₂O, respectively. The average CO₂ evasion rate from surface water was 2.29 ± 0.46 mmol m⁻² d⁻¹ while CH₄ and N₂O evasion rates were 12.89 ± 3.05 and 1.23 ± 0.25 mmol m⁻² d⁻¹ respectively. Therefore, groundwater-derived greenhouse gas fluxes accounted for >100% CO₂ and N₂O and ~43% of CH₄ surface water evasion, indicating SGD is likely an important source of greenhouse gases to surface waters. However, this may be due to observations being performed near the SGD source, which may overestimate its contribution to the wider Sydney Harbour. Over a 20-year time frame, the combined emissions of CH₄ and N₂O from surface waters to the atmosphere accounted for 25% of the total CO₂-equivalent emissions. Although this study gives preliminary insight into SGD and greenhouse gas dynamics in Sydney Harbour, more spatial and temporal resolution sampling is required to fully constrain these processes.

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Dissolved iron exports from an estuary surrounded by coastal wetlands: Can small estuaries be a significant source of Fe to the ocean?

Christian J. Sanders, Isaac R. Santos, Damien T. Maher, Mahmood Sadat-Noori, Bernhard Schnetger, Hans-J. Brumsack

A creek draining a coastal wetland was studied to determine dissolved iron fluxes to the ocean, and whether these fluxes may be driven by submarine groundwater discharge (SGD). Dissolved metals (i.e., Fe, Mn, Ba, and U), natural groundwater tracers ($^{224}$Ra and $^{226}$Ra), and dissolved organic carbon (DOC) were measured every 1 h for 30 h during both summer (wet season) and winter (dry season). The average dissolved Fe concentrations at the mouth of the creek were 8020 and 5630 nM during the summer and winter, respectively. Dissolved Fe concentrations in groundwater were 4060 nM and SGD-derived Fe fluxes were 1.2 mol km$^{-2}$ year$^{-1}$ (catchment area) or 205 mol km$^{-2}$ year$^{-1}$ (creek area). Groundwater seepage played a minor role on the total coastal wetland creek export of Fe to the ocean. The surface water dissolved Fe fluxes to the ocean were approximately $9 \times 10^5$ mol km$^{-2}$ (estuary area) year$^{-1}$ and $\sim 50,000$ mol km$^{-2}$ year$^{-1}$ on a catchment area basis. If our results are comparable to other small estuarine systems and considering the global areas of coastal wetlands (~660,000 km$^2$), short creeks that drain coastal wetlands may discharge a large amount of dissolved Fe to the ocean (32.2 Gmol year$^{-1}$ or ~1.8 Tg year$^{-1}$) which is comparable to the global river estimates (~1.5 Tg year$^{-1}$). The high dissolved Fe concentrations associated with high DOC concentrations and no significant Fe removal within the estuarine gradient seem to be responsible for these large potential Fe fluxes.

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Groundwater seepage as a driver of CO$_2$ evasion in a coastal lake (Lake Ainsworth, NSW, Australia)

Anita K. Perkins · Isaac R. Santos · Mahmood Sadat-Noori · Jackie R. Gatland · Damien T. Maher

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Abstract In recent years, it has become apparent that carbon dioxide (CO$_2$) emissions from inland water bodies and lakes are an important component of the global carbon cycle. Large-scale lake heterotrophy is thought to be a major driver of CO$_2$ production and may mask other processes such as groundwater input. This study uses radon (222Rn, a natural groundwater tracer) to quantify groundwater discharge, and estimates CO$_2$ outgassing to determine the contribution of groundwater-derived CO$_2$ inputs into Lake Ainsworth (New South Wales, Australia). Lake Ainsworth was a source of CO$_2$ to the atmosphere throughout the study period with outgassing rates ranging from 10.6 to 152.3 mmol m$^{-2}$ day$^{-1}$. Annual groundwater fluxes were determined using a radon mass balance equated to about 55 ± 50 % of the total volume of water input (via direct precipitation and groundwater) into the lake. In spite of large uncertainties, groundwater seepage was a source of CO$_2$ supersaturation in Lake Ainsworth equivalent to 13 ± 25 % of total CO$_2$ outgassing rates. Hence, groundwater discharge may need to be considered for carbon budgets of other lakes.